A NOVEL LABORATORY DISPERSIVE AND DISTRIBUTIVE MINIMIXER AND APPLICATIONS

Development of a new minimixer that can duplicate mixing which occurs in a large twin screw extruder.

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Abstract:

The mixing of additives into a plastic is an extremely important step in the plastics industry, necessary for the manufacture of almost every conceivable product. Therefore the costs in developing new products can prove very expensive as the testing is usually carried out using full scale machines, usually using twin screw extruders because they are able to provide good dispersive and distributive mixing. This is particularly important when compounding difficult to disperse additives and nano-additives. What is required is a machine that can replicate the mixing abilities of a twin-screw extruder but on a laboratory scale. There have been attempts by industry to develop smaller machines, such as the Thermo Scientific HAAKE Minilab II Micro Compounder which processes on the scale of 7 cm^3 of material volume. This can be too small for some needs and therefore a machine is required to produce material on the 10g to 100g scale. To this end a laboratory mixer of novel design was devised and its mixing performance was assessed using conductive carbon black and compared against the Thermo Scientific HAAKE Minilab II Micro Compounder, a 19 mm co-rotating twin-screw extruder and a 40 mm co-rotating twin-screw extruder. Carbon black was used because mixing performance can be assessed by measuring

the minimum carbon loading necessary to induce electrical conductivity. It was found that the minimixer was able to induce electrical conductivity at loading of 5.75% but the comparison with the other machines proved difficult as the achievement of the threshold at which semi-conductivity occurred appeared independent of shear rate and mixing duration.

Table of contents

List of figures

List of Tables

List of Charts

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CHAPTER 1: INTRODUCTION

1.1 Introduction

Additives and mixing are words that probably best describe one of the key requirements of the plastics industry. Plastics by themselves are generally "poor" materials, in that they are generally soft materials with little mechanical strength. But their internal structure of molecular chains and how these chains are arranged, make them ideal carriers for additives. As a result the applications and uses for plastics become very broad, thanks to the properties that can be induced. Mixing therefore becomes a key process as additives by definition are used in small quantities, sometimes minute and of order 0.1 wt% and these must be mixed uniformly in the polymer matrix melt - a very viscous material.

The size, shape and orientation of the additive particles also play a great part in how well they will mix into, and their effect on, a polymer [1, 2]. Clearly when these particles are very small (for example nano-scale), they will tend to agglomerate and their dispersion is a big challenge. Therefore as additives are rarely in a single size, size distribution will affect the quality of mixing.

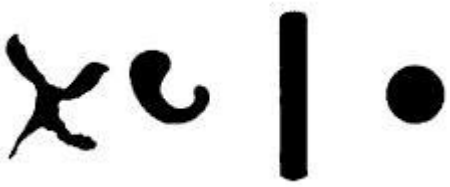


Figure 1.1 Different particle shapes[1]

Shape of course will also be important as mixing requires close interfacial contact and the more complex the shape the more difficult will be the full interfacial contact between the polymer melt and the added particles. Figure 1.1 shows some of the possible shapes that may be encountered for any given additive particle. The first shape is that of an irregular particle with sharp edges and corners. This kind of particle can cause some difficulties as its sharp edges could “cut” the polymer chains of the bulk medium it is being mixed into. The second shape is also irregular but with smooth edges and corners, therefore less likely to “cut” polymer chains, but would still prove difficult to become encapsulated by the bulk polymer. The third shape is that of a rod, has the advantage that it can provide some structural reinforcement if there is orientation of the bulk polymer down its length. The disadvantage of this shape is that the reinforcement it provides is not in all 3-dimentions and therefore unsuitable for such applications. The fourth and final particle is spherical in shape and generally considered the most universally useful and desirable, as it can be easily encapsulated by many polymer chains. In our experiments, we will consider additives that essentially close to spherical, rather than needle or plate type geometry.

Therefore unless the mixing of these particles is thorough (and this will be defined later), there can be no chance for uniformity of properties in the final products, a packaging film for example, a plastic window or a high performance nano-composite. How best to achieve the mixture for the purpose in mind? Which concentrations are required? How does one carry out the formulation at the laboratory scale? Can the laboratory scale be trusted and scaled-up? Or do we require small scale formulation

work? How much does the whole exercise cost and add to the cost of production of the final product? Clearly at the outset we can appreciate the challenges of additive "size". The lower the ultimate particle size of the additive, the more difficult it will be to overcome its tendency to form agglomerates via van der waals forces and thoroughly disperse it within the polymer. Nano-additives are a typical example and they will need to be "intercalated" and "exfoliated" (see Figure 1.2) before their beneficial impact on enhancing properties is observed. Such mixing demands are not easily achievable and the challenge in the industry and in research laboratories alike is to be able to conceive mixing devices that lead to reproducible products with mixing being always consistently complete and uniform.

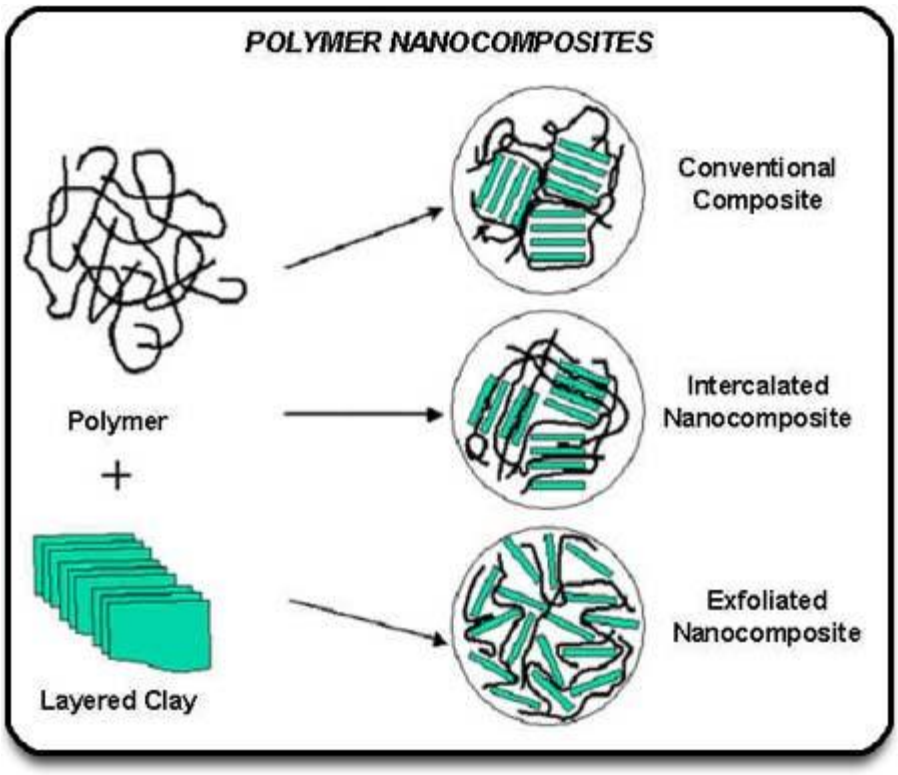


Figure 1.2 Example of Intercalated and exfoliated nanocomposites[3]

For the plastics industry twin-screw extruders are predominantly the machine of choice for the mixing and compounding of additives. This is because they provide regions of intense shear and elongation between two rotating screws, placed in very close contact. These machines come in a variety of designs, which will be discussed in more detail in section 1.3.2.

From a laboratory perspective, twin screw extruders are of course feasible and available at small scales but they are costly to purchase, time consuming to operate and also may require longer mixing time than the design offers. The use of batch mixers like the Brabender helps in this respect and is common. However batch mixers are relatively large and can be unwieldy to discharge the final product. These will also be discussed further in section 1.3.2. As a result of the shortcomings of small twin screw extruders and batch mixers, and with the advent of nanotechnology and the need to experiment over a very large of parameters, there has been in recent years, moves to develop small machines that operate on the scale of 1 – 10g range. Typical examples include the commercially available MiniMAX^{TM} by Custom Scientific Instruments Inc. [4] or the Haake Minilab by Thermoscientific [5]. The MiniMAX takes the form of a heated cup that contains the polymer. A cylindrical rotor then touches the top of the melt and rotates to mix the material in a simple shear flow. The Haake mini lab on the other hand is based on a conical twin-screw design with a recirculation channel and bypass to allow for the extrusion of a strand. Other non-commercial devices have been created such as the “Alberta Polymer Asymmetric minimixer” (APAB) [4] [6]. This device uses a heated cup much like the MiniMAX, in which a specially designed rotor is inserted to mix the polymer melt and

can be used for 1 – 10g of material. An extensional batch mixer (EBM) has also been used by Son [7] which comprises of a heated cylinder with two cylindrical cavities housing a piston. These cavities are connected through a narrow rectangular channel to one another so that the melt can flow between them with the action of the pistons. Mixing is performed by the elongation flow of the polymer between the two chambers. Again this can utilize approximately 1- 10g of material. Another device has been investigated by Yao[8] called the LCMAX 40, which is an axial discharge continuous mixer. This comprises of two parallel and intermeshing two-lobe rotors that are co-rotating in nature, which attempts to combine the features of a continuous mixer and a twin screw extruder in a 40 mm diameter barrel with an axial length of 200 mm. Finally a micro-extruder has been developed by Covas [9] and this is based upon a single screw extruder in design held in a vertical position with the die fixed to a platform and able to extrude a strand in the horizontal direction. This device is able to produce samples of around 10 g in weight, but due to its size requires the raw materials to be in a power or liquid/melt form.

Clearly there are a number of devices in existence that attempt to replicate the mixing typically experienced in industrial scale machines, of which only the LCMAX 40 and Haake Minilab are comparable to industrial scale machines in design. These devices operate in a recirculation mode to allow the mix to experience enough residence time. As the recirculation is via a channel, mixing in the channel is not uniform (zero at the centre line) and this can lead to degradation. The device conceived and built at the University of Bradford under the auspices of an EPSRC research grant to Prof Benkreira and Prof Gale attempts to replicate the mixing of a

co-rotating twin-screw extruder whilst avoiding recirculation via channel. The unique 3 screws design enables the mix to be continuously recirculated by the 3rd screw to the "twin screw" as it will be discussed later. Using this innovative design enables a sizing down of the whole equipment to a laboratory scale that is able to produce samples in the order of 10 – 100 g in size.

This is precisely the perspective of this research: to introduce this innovative design, argue its basis and principle of operation to replicate large scale operation and more importantly test its performance over a range of operating condition and in comparison with other machines, a 19mm TSE, a 40mm TSE and a Haake MiniLab.

In order to appreciate the scope of the polymer mixing industry we begin first by considering the various additives available, their functions and problems encountered during their mixing in polymer melts.

1.2 Additives & their Importance to Plastic Industry

Additives are those materials added in smaller quantities to provide properties otherwise not achievable with the raw material. We use them in all sorts of applications from cooking to developing intricate perfumes or formulating high technology materials such nano-composites, the stuff of 21 century's scientific revolution. Considering plastics, the materials dealt with in this thesis, we can classify additives as follows, essentially according to their function in the final polymer, for example:

- Fillers
- Plasticizers
- Colourants
- Light stabilisers
- Antistatic agents
- Flame retardants
- Nanomaterials

Clearly, the above list of additives is not exhaustive and a very large number of other additives which have developed for specific properties enhancement are available. Also with the advent of nanomaterials, new and more powerful additives are being developed to push further the range of application of polymers in areas that have traditionally use steel, glass, ceramics and other materials perceived to be superior to plastics. A historical perspective must be put here: plastics are new materials, produced in large volume only since the 1950. Their usage and application growth in the past 50 years has been phenomenal and they are now present “everywhere”. Additives and good mixing have been the tools to deliver year in, year out new “plastics” and we are now entering an even more exciting and challenging era, that of nano-composites, which will also review briefly.

Table 1.1 Typical Fillers and Their Effects On Plastics. [10]

	Properties improved													
Fillers	Chemical Resistance	Heat resistance	Dimensional stability	Tensile strength	Stiffness	Impact strength	Hardness	Lubricity	Electrical insulation	Electrical conductivity	Thermal conductivity	Moisture resistance	Processability	Recommended for use in+
Alpha cellulose			*	*					*					S
Alumina	*	*	*											S/P
Aluminum powder										*	*			S
Asbestos	*	*	*		*	*	*		*					S/P
Calcium carbonate		*	*		*		*						*	S/P
Calicium silicate		*	*		*		*							S
Carbon black		*	*		*					*	*		*	S/P
Carbon fiber										*	*			S
Cellulose			*	*	*	*	*							S/P
Cotton (Macerated / chopped fibers)			*	*	*	*	*		*					S
Fibrous glass	*	*	*	*	*	*	*		*			*		S/P
Graphite	*		*	*	*		*	*		*	*			S/P
Jute					*	*								S
Kaolin	*	*	*		*		*	*				*	*	S/P
Kaolin (Calcined)	*	*	*		*		*		*			*	*	S/P
Mica	*	*	*		*		*	*	*			*		S/P
Molybdenum disulphide					*		*	*				*	*	P
Nylon (Macerated / chopped fibers)	*	*	*	*	*	*	*	*	*				*	S/P
Acrylic fiber (Orlon)	*	*	*	*	*	*	*		*			*	*	S/P
Rayon			*	*	*	*	*		*					S
Silica, amorphous									*			*	*	S/P
TFE- fluorocarbon			*		*		*	*						S/P
Talc	*	*	*		*		*	*	*			*	*	S/P
Wood flour			*	*					*					S

+ P = in thermoplastics only; S = in thermosets only; S/P = in both thermoplastics and thermosets.

Fillers:

Most reinforcement additives are bound to the polymer by van der waal forces, and as a result work better if the surface of the particle is smooth and the surface area to surface volume ratios is high[1]. Therefore small spherical particles are considered ideal and this becomes more apparent when the considering the stress concentrations in the polymer as large irregular particles can cause tearing of the polymer chains when a force is applied. Small particles will more uniformly distribute the reinforcement for the same weight of additive. Though small particles are favoured, should they form agglomerates they in effect become large irregular particles and as a result, can cause the problems discussed earlier.

The bonding strength between the particle and the polymer compared to the relative strength of the polymer itself is an important factor. If the polymer-particle bond is weak in comparison to the tensile strength of the bulk polymer, then under low stress conditions the polymer will tend to pull away from the particle, which in turn will result in the occurrence of stress whitening. If the strength of the polymer-particle bond is about equal to that of the polymers tensile strength, then the particle will tend to flow with the polymer during deformation. This would increase the overall tensile strength of the material without altering the yield point. The ultimate elongation will be increased due to the higher strength, but the particle would not interfere with the viscous flow of the material. In the case of a high polymer-particle bond, the polymer finds itself restrained around the particle, resulting in a stronger and more rigid material.

Fillers have a crucial role in plastic manufacturing. As by themselves many plastics have limited applications and uses, but are converted into highly useful products with the addition of a suitable filler. For example the addition of glass fibre into epoxy and polyester resins, which entangle with the polymer chains and provide structural reinforcement as the polymer chains orientate along the length of the fibres, giving rise to a fibre reinforced composite. Another example is the use of carbon fillers to enhance the mechanical properties of rubber. The reinforcement greatly improves the rubbers tensile strength, stiffness, tear resistance, and abrasive resistance. The use carbon black to induce conductivity within plastics is another example, typically where there is a chance that a static charge could be developed such as transporting fluids through a polypropylene pipe. Its fibrous nature enables it to form a network of carbon filaments with the polymer structure, which enable electrons to pass through composite and conduct an electrical charge. The concentration at which this network forms is known at the “percolation threshold” [11]. This threshold can be affected by the quality of mixing experienced, as a poorly mixed composite will require a higher concentration of carbon black to initially form the conductive network. Fillers such as calcium carbonate can be used to make breathable films for applications such as infant nappies. These films can contain around 50% calcium carbonate by weight, which when stretched cause micropores and voids to form in the films structure and allow an increase in water vapour transmission.

Fillers can be divided into two types, particulate and fibrous fillers. Typical fillers and the effects they impart are summarized in Table 1.1. They can be added to perform

one or more functions and the range available is quite considerable, which indicates their importance within the industry.

Plasticizers:

Plasticizers are used to increase the flexibility or plasticity of a polymer. Sometimes they are used as an aid to facilitate processing and in such cases a volatile plasticizer is used that will evaporate off once the final product is produced.

Plasticizers work by interspersing themselves around the polymer, so they can interfere with the chain-chain secondary bonding that occurs in the polymer structure. This interference reduces the inter-chain bonding strength to result in a greater mobility of chain segment and thus in turn an increased flexibility and reduced tensile strength of the polymer. Usually a plasticizer is chosen for its solubility in the polymer as it can penetrate more easily into its structure than a non soluble one. They typically take the form of a lower molecular weight organic material, such as esters of polycarboxylic acids with linear or branched aliphatic alcohols, with a glass transition temperature in the range of 125°K to 225°K. When added to an organic polymer it results in a weight averaging of the glass transition temperature (TG) between the polymer and plasticizer if they are miscible, in effect lowering the glass transition temperature of the polymer.

The glass transition temperature is the temperature below which the physical properties of amorphous materials vary in a manner similar to those of a solid phase (glassy state), and above which amorphous materials behave like liquids (rubbery state). A material's glass transition temperature, TG, is the temperature below which

molecules have little relative mobility. Above TG, the secondary, non-covalent bonds between the polymer chains become weak in comparison to thermal motion, and the polymer becomes rubbery and capable of elastic or plastic deformation without fracture. This effect is illustrated in Figure 1.3.

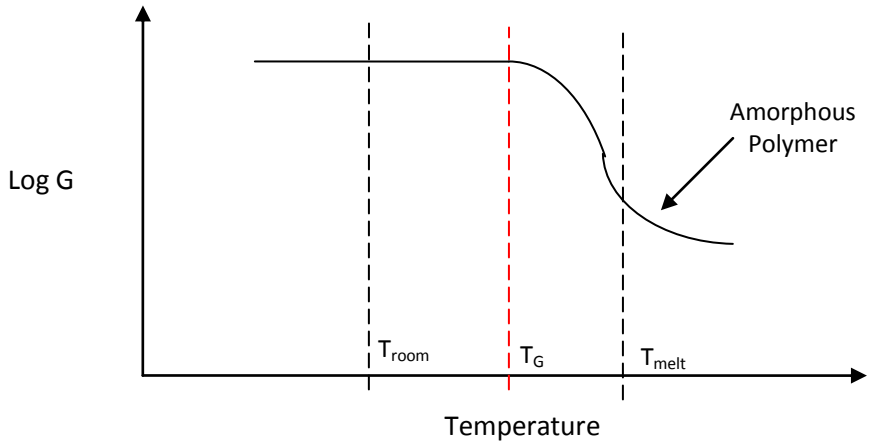


Figure 1.3 The effect of the glass transition temperature

For plastics such as PVC, whose TG value is around 81 °C, the more plasticizer added the lower this transition temperature will be. This means that it will be more flexible though its strength and hardness will decrease as a result.

There are two distinct types, primary and secondary plasticizers. A primary plasticizer is one where a high concentration of polymer is soluble within it. It should also gel the polymer rapidly in the normal processing temperature range and should not exude from the plasticized material. Secondary plasticizers have lower gelation capacity and limited compatibility with the polymer. This resulting in two phases forming at the end of the plasticization process, with one phase slightly plasticized and the other fully plasticized.

Colourants: come in a wide variety of forms, be they inorganic or organic in nature. For transparent materials oil-soluble dyes or organic pigments that have small particle size and refractive indexes near to that of the plastic are used. Typical materials used are barium sulphate and titanium oxide for white, phthalocyanine blues and greens, chrome greens, chrome yellows, quiacridone reds and magentas, as well as carbon black. Flake aluminium is often used for a silver metallic appearance, while lead carbonate or mica is used for pearlescence. There are also many other types which can be use to impart say wood grain effects into the product.

Colour in plastics has many functions, decorative and non-decorative. It can be used to reduce light to protect the contents of a package, for example in medicine bottles. Often it is used simply to protect and conceal as in dashboards, machines housings and pipes. When making opaque mouldings, pigments that absorb or scatter light very well are typically used, such as titanium oxide or carbon black.

Colourants must not catalyze oxidation of the polymer or adversely affect the properties of the material. They also have to withstand the processing and service conditions of the material and be cost effective in how well it covers the material.

Light stabilisers: Most polymers are affected by exposure to light, particularly the ultraviolet (UV) portion of the spectrum, between 300 and 400 nm in wavelength. This is because UV radiation can excite molecules to such an extent that their chemical bond can break. This breakage releases highly reactive radicals that can

destroy more molecules, in a chain reaction. This contributes to degradation of the polymer, especially in the presence of oxygen, which is a normal circumstance for most plastic materials find themselves in. For example, a rubber exposed to UV radiation at 45 °C can oxidise three times faster than if it had been left in the dark at 70 °C. Such light induced degradation reactions can not only discolour the plastic in question, but also have a detrimental effect on mechanical and physical properties.

If the colour of the product is not something of importance, then carbon black is typically used. Not only does it absorb light, it can also react with free-radical species that may form from the degradation reaction. But where colour is an issue there are various types of stabilizer available that create little or no discoloration of the final product. Of these there are four general types of protection:

1) Those that give UV light absorption.
2) Those that quench/reduce the initiation rate for the degradation reaction.
3) Those that convert the Hydroperoxide compounds created within the degradation reaction into more stable forms without creating free radicals.
4) HALS (hindered amine light stabiliser) which “mop up” free radicals as they are generated. Typically called “free radical scavengers”.

This classification is a simplification since most are typically active in more than one way.

UV absorbers basically absorb UV radiation and dissipate it, typically as heat, in a manner that doesn’t lead to photosensitization and doesn’t degrade itself in the process. The main disadvantage with this type of additive is that a certain absorption

thickness within the sample is necessary for good protection. This makes the protection for thin articles moderate at best.

Quenchers are stabilizers that are able to take over energy absorbed from light radiation and dissipate it either as heat or as fluorescent or phosphorescent radiation. Because of how these additives interact with polymer and the degradation reaction, their effect is independent of sample thickness and is specifically useful for films and thin section articles.

Hydroperoxide compounds play an important role in the degradation process caused by UV light exposure, and it is important to transform these into more stable compounds before they experience photolytic cleavage. Complexes of nickel or phosphite with sulphur containing compounds are typically used for this, and are usually combined with UV absorbers for improved performance.

HALS or “Free radical scavengers” are additives that remove the free radical intermediates that are generated during the degradation reaction, hindering its ability to progress. They do this chemically through multiple regeneration of the oxidised species of the amine, the so-called nitroxyl radial. This radical can intervene and regulate the degradation mechanism.

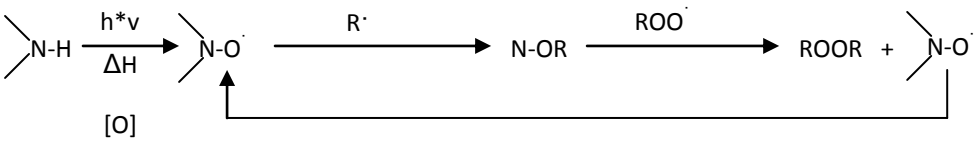


Figure 1.4 General mechanism of action for HALS

Because of this ability to work chemically within the polymer they are suitable for use in applications involving any layer of thickness, although they can lose their effectiveness through interactions with acids.

Antistatic agents: Most plastics are extremely good insulators due to their chemical constitution and this makes them useful in many electrical applications. The disadvantage they have is the tendency to accumulate static electricity on their surfaces. This does not typically discharge quickly due to the low surface conductivity of most plastics. This static can be generated from friction with other non-metallic objects, friction with ambient air flow, and even through the course of process operations such as extrusion, calendaring and the rolling of sheets and films. These static charges can reach up to a few tens of kilovolts in value and present a significant risk to users.

There are two main categories for antistatic agents, external and internal. External agents are applied to the surface of the article in question, usually through some form of coating process. Internal agents are incorporated into the polymer mass as additives, either before or during the moulding process. These internal agents must be only partially miscible so that they migrate slowly to the surface of the plastic material. The concentration of these internal agents typically varies from 0.1% to 10% by weight.

Flame retardants: These additives are typically focussed on being used with thermoplastics and strongly reduce the probability that they will burn in the initiating phase of a fire. It must be noted that in the case of a fire the effectiveness of these retardants depends upon the period of time and the intensity of the fire they are subjected to. Even the most effective retardant cannot resist a strong and long lasting fire. Typical applications are in the protection of electrical cabling, household furniture and textiles.

These additives are defined as chemical compounds that inhibit pyrolysis reactions of polymers or the oxidation reactions implied in combustion. They are divided into three groups:

1) Halogen Compounds
2) Phosphorous Compounds
3) Halogen-antimony synergetic mixtures

The halogen compounds typically are formed from bromine, as these give far better protection that chlorine based ones. With the relative efficiency of the compounds decreasing in the following order:

Aliphatic bromides > aliphatic chlorides = aromatic bromides > aromatic chlorides

These compounds are found to be quite suitable for all types of polyolefins.

Phosphorous compounds on the other hand are more suitable for polar polymers such as PVC, and provide insufficient protection with polyolefins by themselves unless combined with halogen derivatives.

Antimony oxide by itself has a limited flame retarding effect, but when combined with halogens in the system, its effects become quite significant.

The demands on these flame retardant additives are quite considerable as they need to provide a durable effect, while only needing small quantities added to the material.

Nanomaterials: Nano sized minerals such as carbon black and fumed silica have been used in polymers for 50 or more years, but in the last decade much research has gone into new nanomaterials for polymers, such as nanoclays and nanotalcs.

Nanomaterials have very high surface areas compared to naturally occurring minerals. This allows them to improve properties with much lower loading levels than other mineral additives, resulting in final parts with lower weight and density. For example, a nanoclay can have a surface area of around 800 m^2/g, allowing it to be used at levels of 3% – 5% compared to 20% – 30% with a standard filler. As well as improving physical properties they have also been shown to improve thermal stability, flame retardancy and barrier properties.

In the case of barrier properties, nanoclays are finding applications in the packaging industry to help increase the shelf life of food and beverages. The factors that limit

shelf life in this case are the resistance to gas intrusion, typically oxygen and water vapour, and the retention of gases and aromas.

Common approaches have been to coat plastic articles with ultra thin layers of high intrinsic barriers, blend high barrier plastics into medium barrier ones, and the creation of multilayer structures that incorporate barrier layers within them. Each of these has their advantages and disadvantages. In the case of coating and multilayered methods there are issues around adherence between layers or with the coating to the plastic surface. Issues of recyclability arise and in the case of blending barrier plastics, clarity of the plastic when transparency is desired.

Nanoclays are being investigated for improving barrier properties due to their morphology. They form platelets with submicron dimensions but have a thickness of around one nanometer. This grants them a large aspect ratio which is important under the principle of tortuous path migration.

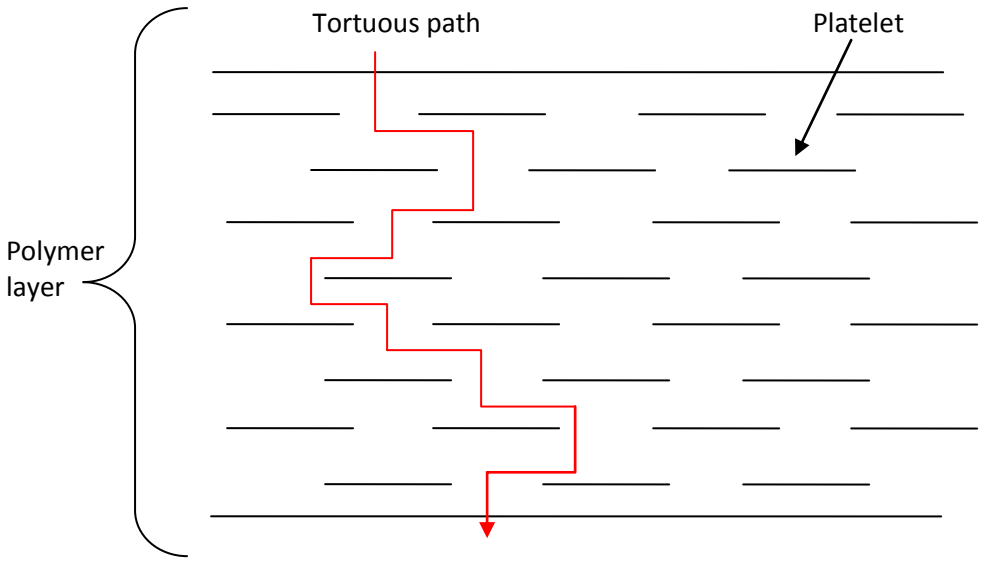


Figure 1.5 Barrier effect of nanoclays within a polymer

The nanoclay settles into the polymer matrix and forms a passive barrier which impedes the diffusion of gases and aromas through the plastic layer or film.

These nanoclays exist as agglomerated bundles of thousands of individual platelets held together by van der waal forces, illustrated in Figure 1.6.

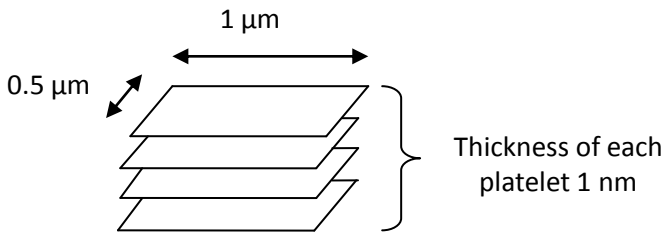


Figure 1.6 Structure of nanoclay agglomerates

So, to achieve optimal barrier properties these agglomerates must be separated into the polymer matrix. This method of separating the platelets has been termed exfoliation, with the resulting compound being called a plastic nanocomposite.

1.3 Mixing & its Importance to Plastic Industry

Mixing is a very important step in the processing industry whether it is for chemical reactions to ensure good reaction or blending to achieve uniformity in properties. With low viscosity fluids, good mixing is usually “easy” as turbulent flow conditions can be achieved and these conditions enable diffusion to be fully effective. With polymer melts and high viscosity fluids or difficult to flow pastes, turbulence cannot

be achieved and the challenge is to develop flow conditions that can ensure all lumps of the material being mixed “meet” again and again to ensure final uniformity and to achieve the required mechanical, physical and chemical properties as well as the desired appearance. Compounding, which is the mixing together of a variety of components (be they different polymers, solid and liquid additives) is regularly used to produce a plastic material with new and improved properties. This offers a far less expensive and practical method for creating new products than the development of new polymers by a chemical means.

In order to fully appreciate the challenges of achieving good mixing with viscous fluids, particularly when small amounts of additives (usually solids or indeed fluids of very different viscosity from the matrix) are used, it is important to study and classify mixing flows, mixing equipment and the all important aspect of scaling up.

1.3.1 Mixing as a Flow Process

Begin by briefly explaining the two fundamental processes of mixing that can be found in the texts [12-15], that of Laminar and Turbulent mixing. From this I’ll lead onto the concepts of dispersive and distributive mixing.

Mixing by definition is an operation that is intended to reduce the non uniformity of the mixture under scrutiny. This can only be accomplished by inducing physical motion of the ingredients in question and in general there are three types that are observed; molecular diffusion, eddy motion and bulk flow. Molecular diffusion is

driven by a concentration gradient, sometimes referred to as chemical potential, and occurs spontaneously. An analogy of this process is that of making a cup of tea. By placing a tea bag in a cup of hot water and leaving it, slowly over time, the clear water begins to darken as the tea diffuses out of the bag and into the water. This continues until the concentration of tea in the water matches the concentration of the tea left in the tea bag.

This process can be enhanced by inducing eddy motion into the fluid. Using the same analogy, this eddy motion is induced by stirring the water with a spoon and reduces the time taken to diffuse the tea molecules into the water and reach the equilibrium in concentration. This superimposing of molecular diffusion and gross random eddy motion or eddy diffusion is inherently faster than molecular diffusion alone and is the dominant mechanism for mixing in turbulent flows and typically labelled as "Turbulent mixing"[12, 15].

This kind of eddy diffusion is not possible in high viscosity fluid where laminar flow dominates as the inertial forces generated tend to die out quickly and become negligible. Similarly molecular diffusion occurs so slowly that it does not contribute much to mixing. Although if the fluid elements involved have been reduced sufficiently in size for their specific areas to become extremely large or that one of the components of the mixture is of a very low molecular weight compared to the others, then molecular diffusion may become a more significant factor in the overall mixing process.

This leaves convective or bulk flow as the dominant mixing mechanism for high viscosity fluids such as polymeric melts[12]. This involves the movement of fluid

particles, aggregates and agglomerates from one spatial location to another. Mixing occurs if the interfacial area between the minor and major component increases or by ensuring the minor component is distributed widely throughout the major component even if the interfacial area between the two has been increased or not.

For polymers this is typically achieved by imposing laminar shear, elongation (stretching), and squeezing (kneading/shearing) deformation to the mixture to increase interfacial area, Figures 1.7 and 1.8 provide representations of how a fluid element thins due to shear and elongational flows.

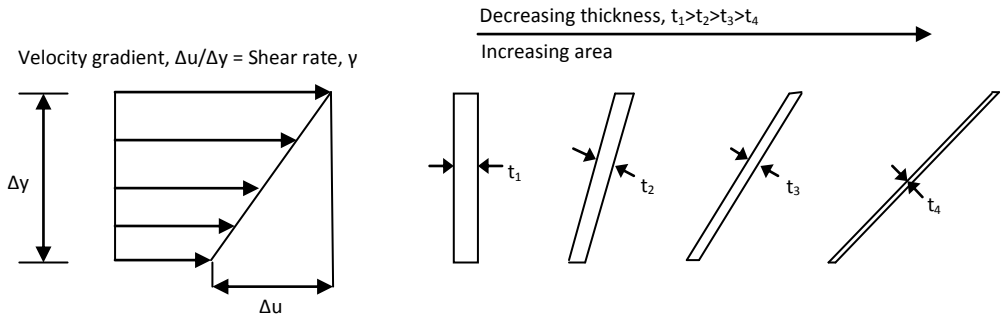


Figure 1.7 Representation of the thinning of fluid elements due to laminar shear flow

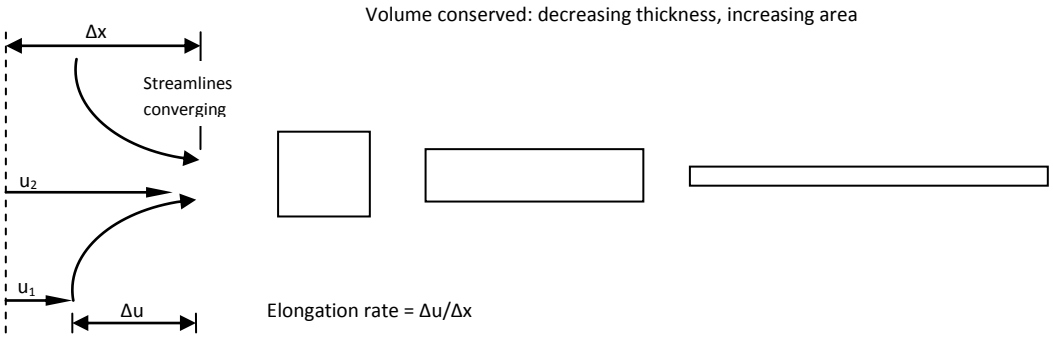


Figure 1.8. Representation of the thinning of fluid elements due to elongational flow

In laminar mixing it is important that the mixture be subjected to permanent deformation or strain. A common practice is by stretching, folding and cutting the flow. This kind of distributive mixing is demonstrated in Figure 1.9. As the mixture is stretched and folded repeatedly the interfacial area of the components increase, resulting in the two components being distributed throughout the volume of the mixture in an ordered manner. This is sometimes referred to as the "Bakers Tranformation" [12] because it mimics the action of a baker kneading dough.

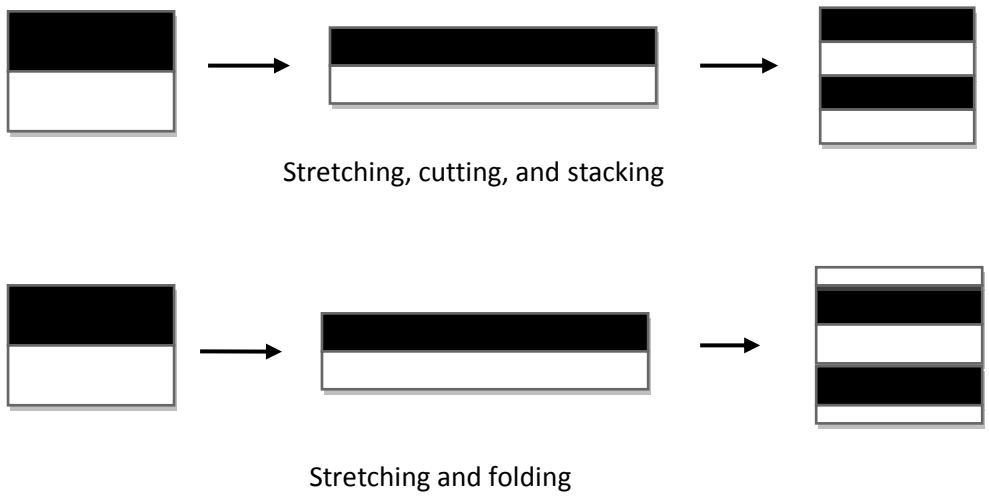


Figure 1.9 Indicates the mixing protocols of stretching-cutting-stacking, and stretching-folding

Laminar mixing imposed by a shear flow is depicted in Figure 1.10 and shows a tube filled with a viscous liquid with a string of spherical tracer blocks of a minor component across the diameter of the tube.

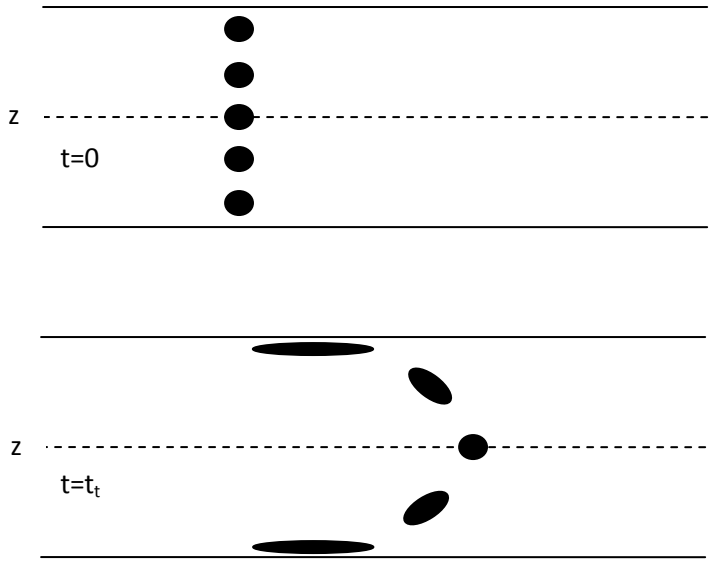


Figure 1.10 Laminar mixing in a lamina pipe flow.

At time t = 0 the blobs are spherical, but as the flow is imposed and time t = t_t passes, the blobs are sheared and distorted. If the shearing and elongational forces applied by the flow are greater than the cohesive forces keeping the blobs together, then these blobs will break up into smaller blobs and be dispersed into the bulk component. This is particularly true in the case of solid agglomerates and aggregates.

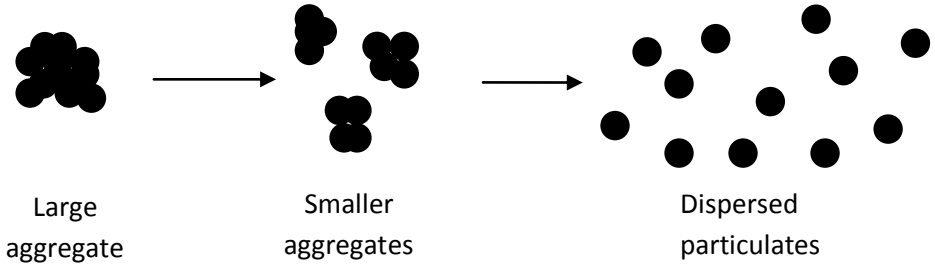


Figure 1.11 A solid aggregate breaking up as the cohesive forces are overcome

This leads onto two key concepts in laminar mixing, especially that of polymers, which is that of distributive mixing and dispersive mixing. As you can see, distributive mixing tends to be a low shear operation of rearranging the bulk fluid in an ordered or random fashion to ensure good spatial uniformity of the minor component. This is sometimes referred to as Extensive mixing. While dispersive mixing is a high shear operation, as it involves the generating forces sufficient to break up and reduce the size of any agglomerates and aggregates present in the mixture. This is sometimes called Intensive mixing.

Figure 1.12 shows a schematic description of Dispersive and Distributive mixing effects.

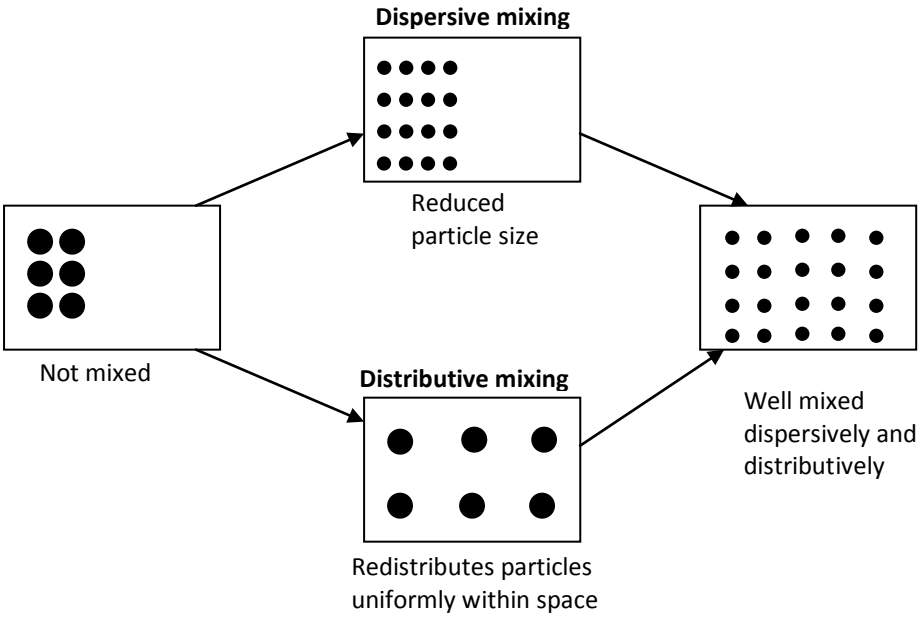


Figure 1.12 Dispersive and Distributive mixing

How well these mixing mechanisms are performed can greatly affect the properties and look of the final product. To this end various types of equipment have been developed over the decades to achieve good mixing within plastics.

To describe in quantifiable manner the extent of these mixing processes Danckwerts[16, 17] devised the concepts of “scale of segregation” and “intensity of segregation” as a means to measure the effects of mixing and this work is referred to by Gogos[12] and Toor[18].

1.3.2 Mixing equipment: A brief history

The machinery used today is based upon the machines first developed during the industrial revolution to process natural rubber and in the case of some machines, they are relatively unchanged in design. Table 1.2 has been adapted from Tadmor and Gogos[12] and lists a brief history of some of the machines that have been developed for the plastics and rubber industry over the past 200 years, starting with the likes of the “The Pickle” invented by Mr T. Hancock in 1820 to reclaim natural rubber, and continuing on to such as the first form of extruder, the ram extruder in 1845, then screw extruders in 1860, all the way up to recent times and the ZSK extruders by Erdmenger.

Table 1.2 A brief history of mixing equipment in the plastics industry.

Machine	Process	Inventor	Date	Comments
The 'Pickle'	Batch mixing	T. Hancock	1820	Reclaim rubber
Roll mill	Batch mixing	E. Chaffe	1836	Steam-heated rolls
Calender	Coating and sheet forming	E. Chaffe	1836	Coating cloth and leather
Ram extruder	Extrusion	H. Bewly & R. Brooman	1845	
Screw extruder	Extrusion	A.G. Dewolfe	1860	Attributed to
		PhoenixGummiwerke	1873	Archimedes for
		W. Kiel & J. Prior	1876	water pumping.
		M. Gray	1879	This has become
		F. Shaw	1879	the most important
		J. Royle	1880	machine for plastics and rubber.
Injection moulding	Injection moulding	J. W. Hyatt	1872	Celluloid
Counterrotating, nonintermeshing twin screw extruder	Extrusion	P. Pfleiderer	1881	
Gear pump	Extrusion	W. Smith	1887	
Co-rotating, intermeshing twin screw extruder	Mixing & extrusion	R. W. Easton	1916	
The Banbury	Batch mixing	F. H. Banbury	1916	Developed for rubber mixing
Counterrotating, intermeshing twin screw extruder	Extrusion	A. Olier	1912	Positive displacement pump
Knetwolf	Twin rotor mixing	W. Ellerman	1941	
Ko-Kneader	Mixing & Extrusion	H. List	1945	
Triangular kneading blocks	Continuous mixing	R. Erdmenger	1949	Usedin the ZSK extruders
In-line reciprocating injection moulding	Injection moulding	W. H. Wilert	1952	Replaced ram injection moulding
ZSK	Continuous mixing & extrusion	R. Erdmenger, G. Fahr & H. Ocker	1955	Co-rotating inter meshing twin screw extruder with mixing elements
Transfermix	Continous mixing	N. C. Parshall & P. Geyer	1956	Single screw in a barrel in which screw-type channel is cut
Normal stress extruder	Extrusion	B. Maxwell & A. J. Scalora	1959	Two disks in relative rotation
Continuous ram extruder	Extrusion	R. F. Westover	1962	Reciprocating rams
Slider-pad extruder	Extrusion	R. F. Westover	1962	Slider pads rotating on stationary disk
FCM	Continuous mixing	P. Hold et al.	1969	Continuous Banbury
Diskpack	Extrusion	Z. Tadmor	1979	Co-rotating disk processor

1.3.2.1 Batch mixers

The first documented machine was a rubber masticator, which was developed in 1820 by Thomas Hancock to reclaim scraps of processed natural rubber. This was followed by the development of the two-roll mill by Edwin Chaffe, for the mixing of additives into rubber.

Two-Roll mill: This works by having two rollers rotating in opposite directions. The front roller is typically hot and rotating slowly, while the back roller is cold and rotating relatively fast. See figure 1.13.

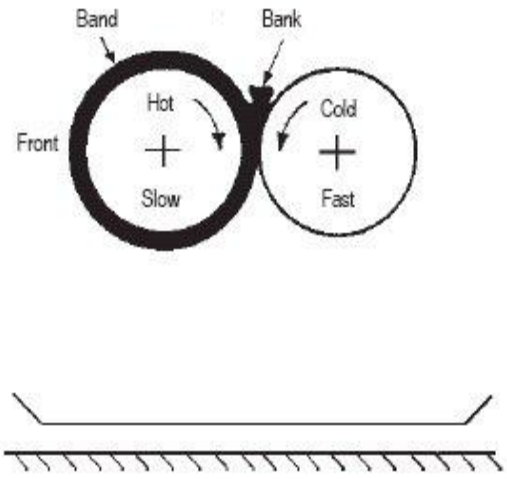


Figure 1.13 Two-roll mill[19]

The rubber tends to gather on the hot slow roll, the front roll, in the form of a continuous band with the excess forming a 'bank' which churns around the nip between the rollers. It may take a few attempts for the rubber to be conditioned to the state when it will adhere to the roll. In which case it is necessary to stretch under the roll, pull out an end and press it to the face of the front roll to help it up over the crown and back into the nip. This manoeuvre may have to be repeated

several times before the band is established. On occasions, difficult stock, or incorrect heating (or cooling) may cause the rubber to collect on the back roll, in which case it must be cut across the face of the back roll and allowed to drop into the tray. Then it can be picked up from the tray and helped over the front roll. The physical characteristics of certain synthetic rubbers are such that the material tends to gather on the 'cold fast' roller, i.e. the back roll. In a few cases the characteristic is so pronounced that they have to be worked entirely on the back roll. To achieve homogeneity in the rubber during mastication and even dispersion and incorporation of ingredients when mixing, the rubber may be 'turned' and 'folded' or 'crossed' in various ways. One method is to cut a continuous strip, about half the width of the band and allow the leading end to drop into the tray, see figure 1.14 and figure 1.15. At a predetermined stage the operator ceases to cut, and the stock pile picks itself up again back into the nip. Another method is to cut and roll up a long strip to form a 'dolly' and to feed this end back into the nip.

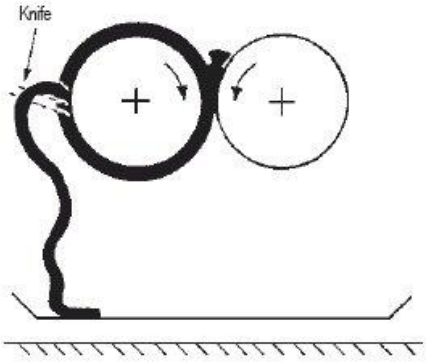


Figure 1.14 Strip cut on Roll Mill[19]

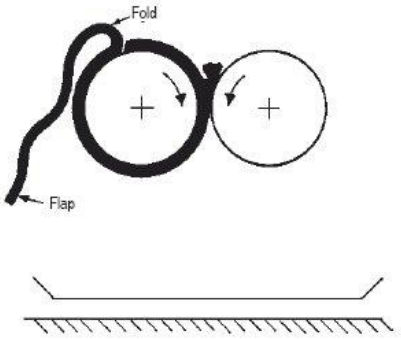


Figure 1.15 Strip folded and fed back into nip[19]

As the rubber is masticated into a soft mass by the heat from the rolls it can be worked at the nip in which state it can absorb the various additives either in the form of powders or already mixed with rubber in the form of 'master batches'. The powders are generally fed by shovel or scoop, any spillage being caught by the tray where it is swept up and returned to the nip. Certain powders, either by reason of their small weight in comparison to the total batch (such as certain vulcanising agents) or difficulty in dispersion (such as pigments) may be actually rubbed on by hand onto the rubber as it runs on the front roll. All of this is a labour intensive set of operations.

Banbury mixer: The need to mix fine particle additives, such as carbon black, into rubbers made the mixing in open roll mills undesirable. This led to the development of enclosed interior mixers, specifically the Banbury type mixer. This machine, even now, is considered to be the workhorse for rubber processing.

The machine, see figure 1.16, comprises of a figure eight shaped chamber with two spiral lobed rotors, one set in each half if the chamber. There is a small clearance between each of the rotors and the walls of the mixing chamber. The rotors can be operated at different speeds if required. Material is fed into the mixing chamber via a vertical chute, in which a ram is located to force material down and seal the mixing chamber. Both the rotors and the mixing chamber walls are temperature controlled, with a discharge door at the bottom of the machine for the homogenized material. During operation the material is swept around the walls of the chamber and exchanged between each of the rotating lobes, causing it to experience constant shearing and folding. The friction generated within the material can be quite significant, causing addition heat generation depending on the speeds of the rotors.

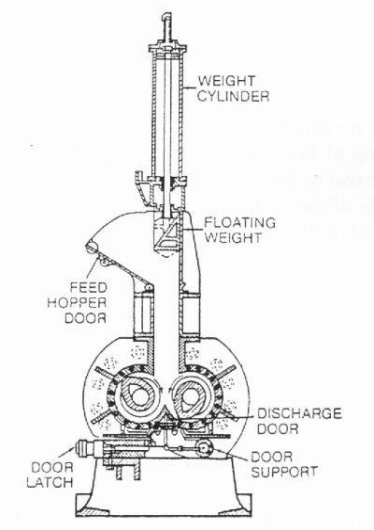


Figure 1.16 Banbury Type Mixer

Nowadays, most of the modern processing machinery have at their core a screw or screw type rotor. This is mainly due to the success of the single and twin screw extruders, the only exceptions being that of roll mills and calenders.

1.3.2.2 Screw extruders

The first extruder appeared in 1845 with the creation of the ram extruder by Henry Bewly and Richard Brooman. This was used to produce the submarine cable between Dover and Calais and later for the first transatlantic cable between the United Kingdom and the USA. This need for continuous extrusion of wires and cables led onto the development of the single screw extruder (SSE), which rapidly replaced the non continuous ram extruders. Essentially, these machines originate from the classical single screw design, see Figure1.17. This is very effective in that in one machine, melting, mixing, pumping and shaping is achieved in a continuous manner.

Single screw extruder

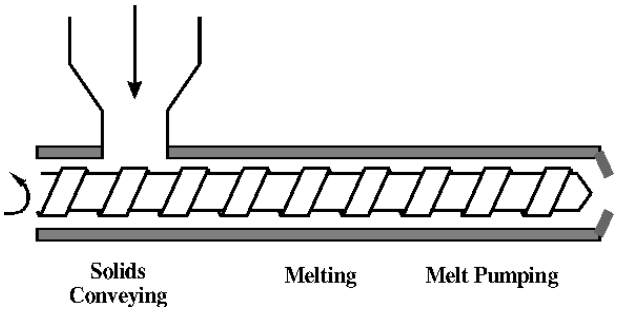


Figure 1.17 Single screw extruder diagram[20]

In its basic form a single screw comprises of three distinct zones. A solids conveying zone, where solid pellets or powders are charged to the extruder and conveyed down the barrel. A melting zone, in which the solid material is heated so that it begins to form a viscous melt. Finally there is a pumping/metering zone leading up to the die of the extruder. There is some variation in this basic screw design to ensure complete melting of the solid material.

This can take the form of additional flights in the screw, changing in screw pitch and depth, multiple stages and the addition of single or double barrier flights. These can be seen in figures 1.18 to 1.21. Barrier flights divide the solid and melt channels such that the clearance over the barrier flight will only allow melt to enter into this channel. This has the tendency to cause the screw to bend towards the barrel and causing excessive wear on the screw. This was reduced in the case of double barrier screw design as it is double flighted and both flights have their own barrier flight. As a result this balances the screw and causes the bending forces to cancel each other out and prevent excessive wear in the screw

Standard screw with additional flight in the feed section

Variable pitch extruder screw with increasing pitch

Variable pitch extruder screw with reducing pitch

Figure 1.18 Typical basic screw designs

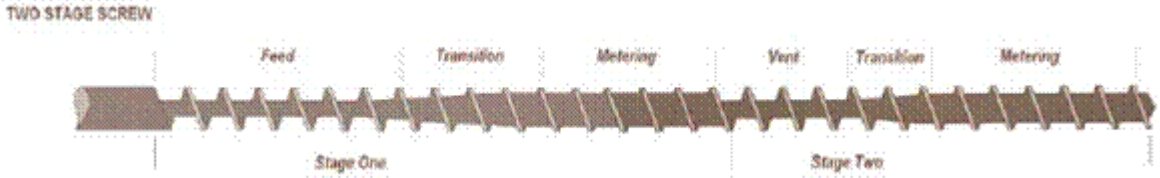


Figure 1.19 Two stage single screw

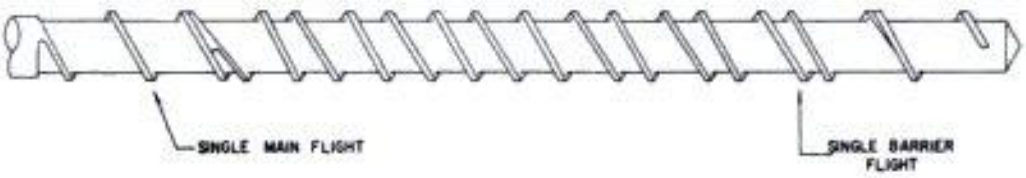


Figure 1.20 Single barrier flights screw[14]

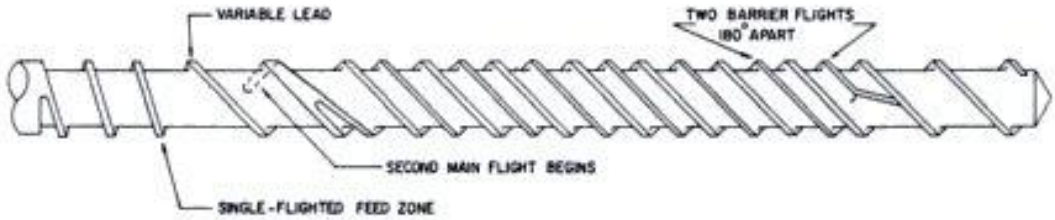


Figure 1.21 Double barrier flights screw[14]

Because mixing is at the heart of the operation, the screw design evolved over the years to enhance dispersive mixing (see figure 1.22 with typical screw designs) leading eventually to the twin-screw extruder the norm in today's demanding industrial environment. Without the addition of mixing sections in the screw, the mixing of additives into the melt takes place in the melt film adjacent to the barrel. Some of the pellets enter the melt film at the trailing side of the flight, others only at the melt pool. The closer the pellet is to the melt pool, the less it is exposed to the high shear rate of the barrel interface. The melt in the melt pool is therefore inhomogeneous. Therefore to improve melt uniformity, intimate mixing of the melt pool is necessary. This is achieved by strategic placement of various types of mixing element before and in the pumping/metering zone of the screw.

These extruder mixers can range from very simple designs such as the addition of pins and barrier rings onto the screw, to more complex designs such as the fluted barrier-type or the cavity transfer mixer (CTM). In the case of the CTM this device is installed at the end of the screw, where the melt is pushed through a rotor and stationary stator. Both the rotor and stator hold cavities so that as the rotor rotates material is transferred between cavities, see figure 1.23. Naturally these can cause significant pressure drops across the screw. Therefore good screw design is essential to balance the need for efficient solid transport, melting and mixing before discharge.

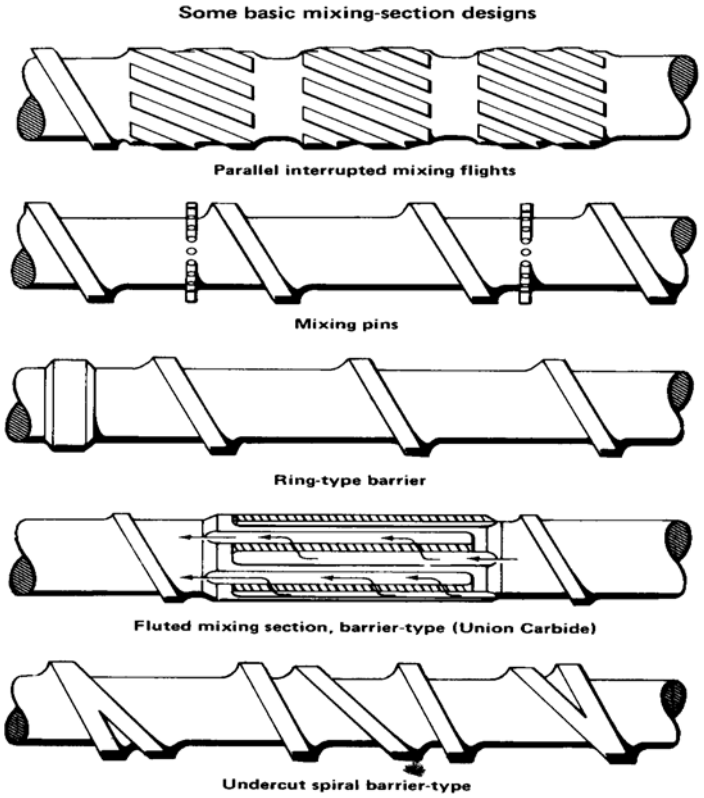


Figure 1.22 Examples of single screw mixer designs

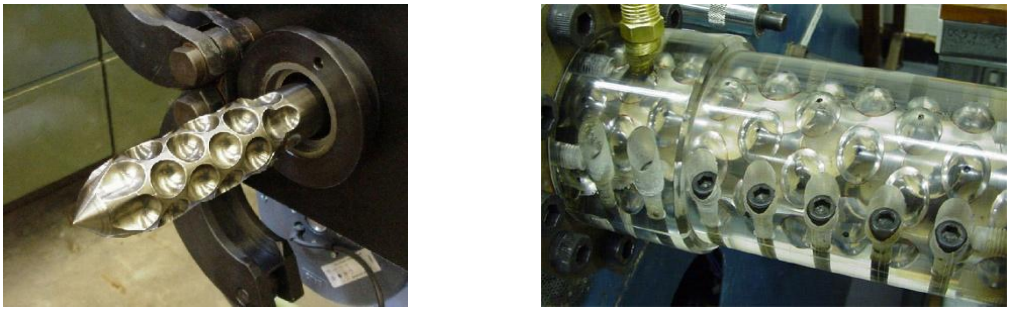


Figure 1.23 Transparent CTM, clearly showing Cavities in Rotor and Stator[21]

Twin-screw Extruders

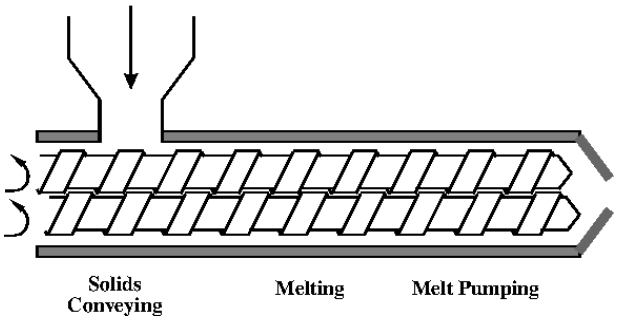


Figure 1.24 Twin-screw extruder diagram[22]

In 1881, the first non-intermeshing, counter rotating twin screw extruder (TSE) was developed by Paul Pfleiderer. The intermeshing counterpart was not developed until 1916 by R. W. Easton. The ZSK-type co-rotating, intermeshing extruders were developed in 1955 and proved to be extremely popular, machines based on these today are still widely used for continuous mixing and extrusion of plastics. Their advantage of self wiping screws enabled them to process a wide variety of materials.

Basically, the layout of a twin-screw extruder is not different to a single screw extruder, see Figure 1.24. You still have a solids conveying section, a melt section and a melt pumping/metering section. Where the designs differ is that instead of one screw present in the barrel you have two, with material constantly interchanging between the two and increasing the dispersive mixing capabilities of the machine.

Intermeshing of the screws increases this capability further, so the closer the screws intermesh, the higher the degree of dispersive mixing that occurs. This comes with the disadvantage that the close the screws are intermeshed, the more power that is required to drive the screws.

From figure 1.25 it can be seen that there two types of intermeshing twin-screw extruder in use, “Co-rotating” and “Counter rotating”. In co-rotating twinscrews the flights of both screws follow the same directional alignment, so that material flows easily from one side to the other as screws rotate in the same direction, effectively extending the flow path of the melt.

In a counter rotating twin-screw, the flights of one screw is arranged into the mirror opposite of the other. As the screws rotate in the opposite direction, the bulk flow of the melt is still pushed in the same direction down the barrel. This kind of kind of intermeshing has the effect of causing material contained in the flights of both screws to be swept into the center of the barrel and into the nip between both of the screws. This causes churning and folding of the melt as it flows down the barrel towards the die.

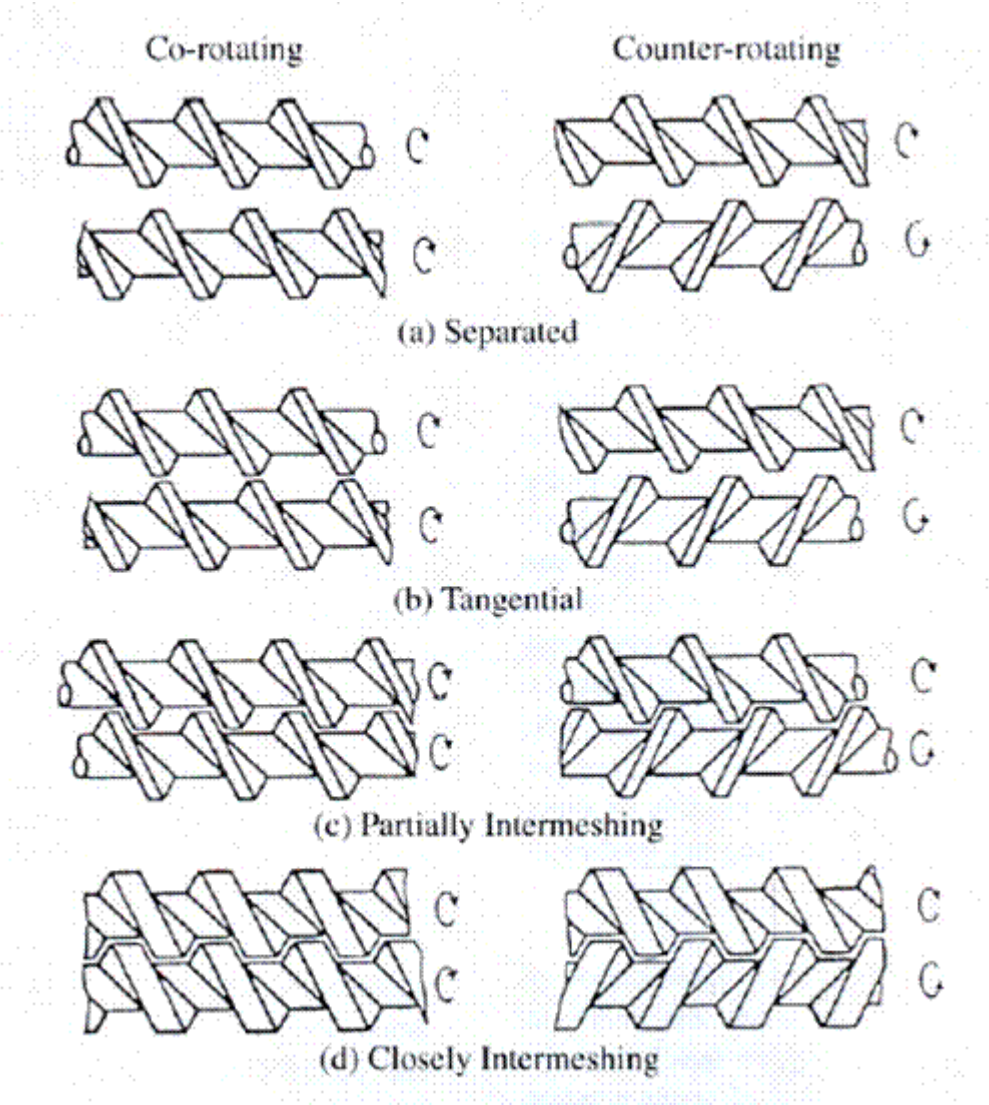


Figure 1.25 Degree of intermeshing capable in Twin-screw Extruders

Just the fact that the screws are intermeshing is not enough to meeting most mixing requirements. The incorporation of “Kneading blocks”, “Mixing lobes” and specialized screw sections into the design for intensive and extensive mixing, coupled with their segmented design allowed them to be matched to the required processing needs, as it is not possible to use similar mixing designs to that found in a single screw extruder.

Mixing lobes come in all shapes and sizes, ranging from single lobes, bi-lobal, tri-lobal and more. These lobes can be installed so that each one is rotated with an offset to the previous lobe, creating a spiral down the section like the Werner & Pfleiderer designs [Ref]. Others may be installed with alternate 90 degree offsets. Some mixing sections maybe toothed rings, or even cam shaped screw flights. Figures 1.26 and 1.27 shows some examples of the many types of mixing elements available these days.

Figure 1.26 Examples of mixing segments for twin-screw extruders. [23]

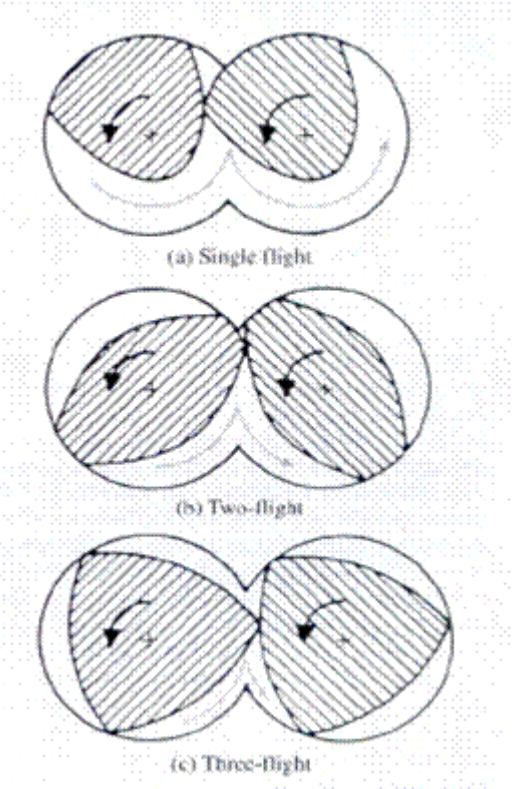


Figure 1.27 Examples of multiple flight lobes in a co-rotating twin-screw

An almost infinite number of combinations of twin-screw arrangements are possible, making the design of such a machine almost an art-form, requiring years of experience.

Conical Twin-screw

Other multiple screw designs have been developed, namely the conical twin-screw extruder. This comprises of two intermeshing screws with a large bore at the feed section and gradually tapering towards the die. As with standard twin-screw extruders, these can be co-rotating or counter rotating in design. The conical design generates compression continually down the length of the barrel, causing material to be kneaded and sheared along the profile of the screws. This kind of mixing has been

dubbed “Profile Kneading” and reduces the need for the addition of mixing sections found typically in standard twin-screw extruders. Figure 1.28 shows typical conical screws.

Figure 1.28 Examples of Counter rotating Conical Twin-screw designs[24]

1.3.3 Mixing new challenges

In today’s world items containing plastic materials are prolific, ranging from simple plates and tubs, to more complex structures such as moulded car parts. All of these require uniform mixing of the additives described earlier in section 1.2. The main

focus now is on making use of nano materials and incorporating these highly expensive additives into plastic products. To work effectively these materials have to be distributed and dispersed uniformly throughout the polymer melt, the agglomerates of these materials can significantly affect the properties desired. This is especially important with nano-additives that need to be intercalated and exfoliated (see figure 1.2) so that the nano additive nestles within the molecular structure of the bulk material.

1.4 Current Practice for Formulating Plastic Compounds

1.4.1 Industrial Practice

Creating new formulations for plastic compounds is in some ways considered a "black art", as it involves a deep understanding in what properties you wish the plastic to exhibit and have considerable experience in knowing how the incorporation of additives affect plastics. It is not always the simple case of adding one additive, a range of additives may be needed, some of which will offset unwanted side effects from some of the other additives. There is also the problem that scale-up from small machines to larger extruders can be problematic, as conditions that might be considered insignificant in the smaller machine, may be quite significant in the larger extruder. Plus there is the issue of keeping the effect of shear the same within each machine, feeding materials in a similar manner, having similar screw arrangements, etc. So getting things right in only a few runs is quite important, especially due to the size of the machines and the throughputs they can produce. Any error can be quite costly, not only in materials, but in time and energy, especially when you are using machines that run in the order of 100's of kilos per

hour and one needs to take representative samples to check the quality until customers requirements are met. It is not unusual to have a certain product dedicated to specific machines, because the same formulation does not necessarily work as well in another machine with a similar setup and operating conditions.

1.4.2 Academic/Laboratory Practice

Laboratories and academic departments have some limited options at their disposal. At one end of the scale they can make use of industrial extruders that process kilos of material ranging from 1-10 kg/hr at a time. These can offer much data but still fall foul of ensuring they can obtain sufficient material to test and the cost of running full scale machines. As discussed earlier at the smaller end of the scale there are devices such as the MiniMax, "Alberta Polymer Asymmetric minimixer" (APAB), the extensional batchmixer (EBM), the LCMAX 40, the Micro extruder and the Thermo Scientific HAAKE Minilab II Micro Compounder[5]. The Minilab requires only 7 cm^3 of material volume to conduct its measurements, which can be an advantage when only small quantities of expensive material are available, See Figure 1.29. The device can perform some rheological measurements and extrude a thin strand. These strands though are usually too thin and of insufficient quantity to perform other offline tests, such as tensile strength tests. The device also incorporates a recirculation channel so that it can be operated in a closed batch system to allow control of residence times, but with some viscous materials this channel offers an area were the fluid will experience a reduction in flow velocity and the possibility of

thermal degradation and provide an opportunity for filler/fiber particles to re-agglomerate.

Figure 1.29 Thermo Scientific HAAKE MiniLab II Micro Compounder[5]

The MiniMax and APAB are “closed cup” in design and advantageous when only a tiny quantity of material is available but as such have the problem of discharging the material much like that experienced in batch mixers like the Banbury mixer.

1.4.3 Scale up & Challenges

Scaling up from a smaller machine to a larger one can be very tricky. Small problems that appear insignificant within the smaller machine can become quite significant within the larger one.

When scaling up any limiting factor, whether product or process related, needs to be identified and monitored. For example, the property profile at low throughput may exhibit high impact and flexural properties. But at higher throughputs, where the

melt temperature is higher due to more shear heat being generated, a reduction in molecular weight occurs and thus a reduction in impact properties. In the larger extruder the desired properties may only be equivalent to those found in the smaller extruder if it runs at low throughputs as the melt temperature is low enough. It can be possible to increase throughput and maintain melt temperature by altering the screw design, but this may result in poor mixing and cause some other product deficiency. There are many other limiting factors that can affect scale up such as:-

- Heat input and control
- Motor power
- Downstream equipment
- Feed capacity

Giles [13] describes a method of assessing the probable throughput that might be experienced when scaling up from one twin screw extruder size to another. The method involved assessing three main steps:-

1) Volumetric scale up
2) Power requirements for the motor
3) Scale up of heat transfer

For each of these steps a simple equation is used based upon the diameters of the extruders as well as assuming the following assumptions:-

1) Similar screw designs and geometries
2) Similar screw speeds as measured by the element tip speed
3) Same percentage fill and average residence time within the extruder

The equations can be applied to extruders which have the same outer-to-inner diameter ratio for the screw elements (Do/Di ratio) more easily than those that do not.

1.5 Aim and Objectives of the Research

The aim of the research then becomes:

- To develop a laboratory scale mini-mixer which uses a small quantity of material, typically 10-40g, but which is capable of replication of the intense mixing which occurs in the large machines used in industry, typically co-rotating screw extruders.

The objectives are thus the steps undertaken to achieve this aim and they are:

1) Review the literature on mixing in the plastic industry and distil from it the essential equipment design requirements for good mixing. This area is very well documented and we will be guided by a century of work progress in twin screw extrusion
2) Use the essential design features of good mixing and develop the minimixer bearing in mind the need for replicating conditions in the larger scale operation. Here both mixing stresses and mixing time have to be controlled.
3) Build the mini-mixer, preferably in a modular construction to achieve the flexibility required for optimising the final design
4) Test the operation of the minimixer with materials typical of those used in the plastic industry

5) Compare the performance of this mini-mixer with competing laboratory devices and co-rotating twin extruders at larger scale
6) Underpin the operation of the minimixer with a theoretical basis, largely based on steps 1 and 2.

Chapter 2: Literature survey

2.1 Introduction

This chapter reviews work in the literature that enabled us to understand the design of the mini mixer used in this research. Clearly the review which follows is unusual in the sense that we are more interested in design and development of small devices, than the principles of mixing which were discussed in chapter 1, not that these are not important. In this literature review the design and operation of Single and Twin-screw extruders are discussed and establish that Twin-screw Extrusion is the equipment of choice for this application.

Having explained the principles, we then followed on to understand scaling as our research is concerned with a small device. We identify the residence time as being the key factor that has led previous researches to develop small devices with recirculation section built into them. We will demonstrate at the end of this review that the merit of our new proposed design is that we create recirculation directly without the need for a separate re-circulating section, which exposes the material to non uniform mixing, possible re-agglomeration of material and probably degradation.

2.2 Design

2.2.1 Single screw extruders

As discussed briefly in the introductory chapter, polymer processing in a single screw extrusion is inadequate to provide suitable distributive and dispersive mixing. This is because in essence a single screw extruder is essentially a pumping mechanism unless the provision of distributive and dispersive devices are incorporated either at the end of the screw or engineered within the screw itself.

This can be seen in melting and conveying mechanisms for single screw extruders. The melting of the polymer pellets primarily comes from them being sheared against the barrel wall. Although heat conduction does play its part, polymers are typically poor thermal conductors. Figure 2.6 shows a schematic model of the melting process.

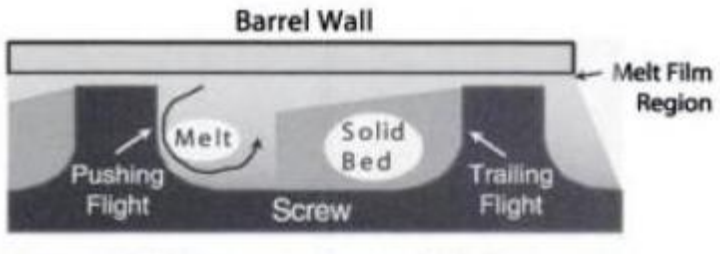


Figure 2.1 Melting model for a single screw extruder. [13]

As the leading edge of the flight pushes the solid pellets forward and against the barrel wall they are sheared and the heat generated by the friction caused results in a thin film of polymer melt to form. The solid bed is compressed by the conveying pressure and the increasing screw root diameter as polymer is conveyed forwards. In

the thin film region between the barrel wall and solid bed, more polymer melts due to a combination of shear, through the viscous heat generated at the boundary between the melt film and solid bed, and barrel heating. The melt is then scraped off the barrel wall by the pushing flight and forms a melt pool which forces the solid bed forwards against the trailing flight. This melt pool grows in size as the more of the polymer melts from the heat generated by the melt film being sheared between the solid bed and barrel wall. Figure 2.7 schematically shows this mechanism as the polymer travels down the feed and transition zones of the screw.

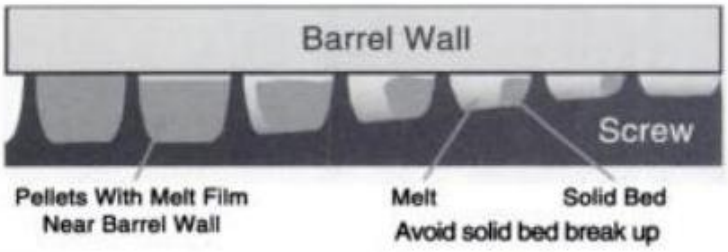


Figure 2.2 Melt mechanise as the polymers travel down the barrel length[13]

Once the polymer has melted it is then conveyed down the remainder of the screw towards the die. If there are no further modifications to the screw geometry the path the melt takes can be described as follows [13].

The model assumes the barrel rotates and the screw remains stationary, so that it is taken from the perspective of a point in the melt close to the barrel wall. The melt at this point moves in the rotational direction of the barrel until it meets the pushing flight of the screw. As the barrel continues its rotation, the polymer that is in contact with the pushing flight is forced down along this flight and across the channel until it meets the trailing flight and is turned up towards the barrel wall once more. As the

polymer approaches the wall it begins to follow the barrels rotation once more until it meets the next pushing flight. This spiralling flow path shears the melt in the metering zone of the screw. Therefore, unless additional mixing sections are incorporated, a single screw extruder performs poorly as a mixer. Therefore you can imagine that if there are any un-melted polymer pellets or agglomerates of additives present, they will likely just be carried along by this spiralling flow until they reach the die, and not be fully melted/mixed into the melt.

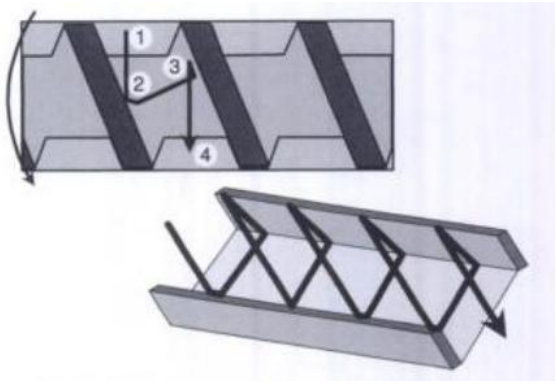


Figure 2.3 Melt flowpath in a single screw extruder. [13]

Hence the need to modify the single screw extruder to include distributives and dispersive mixing devices, either tagged on at the end of the single screw or engineering within the screw itself some of which was discussed in Chapter 1. The literature is full of studies on the mixing capabilities of single screw of extruders and their mixing devices, such as the work done by Erwin[25, 26], , Benkreira [27]to name but a few. The key point in these studies is the nature of mixing and how it develops along the length of the extruder from the melting zone to the pumping zone. Benkreira [19] for example argued that mixing on melting in single screw extrusion is very important as the melt layer between the solid bed and the screw is small enough to create high shear. In general, mixing in single screw extrusion is

considered to be controlled after the solid has melted, i.e. residence time distribution during melt mixing and pumping as well shear rate are the controlling factors.

2.2.2 Twin-screw extruders

This need for dispersive and distributive mixing capabilities naturally leads onto the design of the twin screw extruder, which is capable of creating large shear stresses and elongation flow. As described in chapter 1, twin-screw extruders can be co-rotating or counter-rotating with either intermeshing or non-intermeshing screws. High speed co-rotating twin-screws are the norm for compounding with additives and therefore the focus has been on this design. In co-rotating extruders both screws rotate in the same direction, be it clockwise or anti-clockwise rotation. In fully intermeshing co-rotating extruders the polymer flow makes a figure of eight pattern as the material does not pass between the screws but flows around them as show in figure 2.9. The high pressure and low pressure regions generated by the flow are clearly shown. But the material flow and the shearing it experiences is also dependant on the degree of intermeshing of the screws and this can been seen in Table 2.1

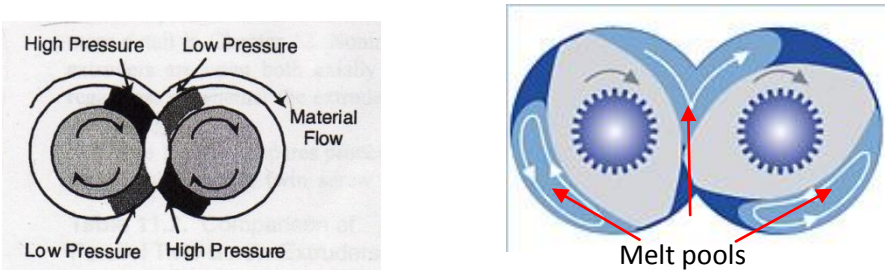
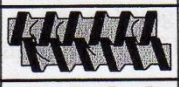
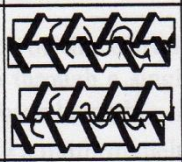
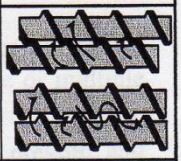


Figure 2.4 Material flow in co-rotating screws[13, 28]

Table 2.1 Material flow based upon the degree of intermeshing[13]

Screw Distance	Material Flow	Counterrotating	Corotating
Fully Intermeshing	Closed to Length and Cross		Impossible
	Open to Length Closed to Cross	Impossible	
	Open to Length and Cross	Possible, Not Practical	Kneading Blocks and Gear Mixers
Partially Intermeshing	Open to Length Closed to Cross		Impossible
	Open to Length and Cross		
Noninter-meshing	Open to Length and Cross		

The designs shown are described as being either open or closed in a certain direction and this has been defined as follows.

1. If material can flow in the axial or longitudinal direction from the feed towards the die, then the screw is classed as open in the length direction.
2. If the screw is closed to material flow in the axial direction then the length direction it is classed as closed.
3. In the cross or cross-machine direction, it is open if the material can flow around a particular screw channel.

In fully intermeshing co-rotating screws this ability to cross flow is not possible as material cannot pass in-between the screws, only around them.

This degree of intermeshing also affects the degree of mixing that naturally occurs as the material progresses through the extruder. If both the length and cross-flow directions are open, then distributive mixing can be expected with poor pressure

generation occurring. If the length direction is open but the cross flow is closed then a mixture of distributive and dispersive mixing is expected with poor pressure generation occurring. If both directions are closed then dispersive mixing occurs with good pressure generation. This mixing caused by the material flowing through the machine is an improvement on that of the single screw extruders, but still does not always meet the mixing requirements desired. So as before, a mixing section is typically incorporated into the screw design. These usually take the form of kneading blocks of various shapes and sizes, placed in various orientations. A mixture of narrow and wide kneading blocks are used, with narrow ones providing better distributive mixing as the material flow in and around the blocks. The wider ones provide better dispersive mixing as the material has a tendency to flow over the top of the block and be squeezed through the narrow gap that forms between it and the barrel wall [13].

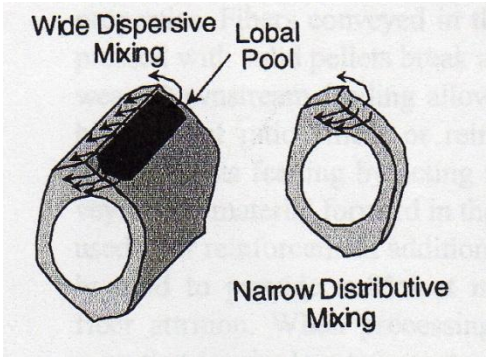


Figure 2.5 Lobal pool flow around Wide and Narrow kneading blocks[13]

This then leads onto the concept of the available free volume provided by the intermeshing screw elements [13], which is the volume within the extruder barrel available for pellets, powder, reinforcements, fillers, and/or polymer melt. This can be calculated for any given extruder using the following equation.

$$V_o = A_o \times L \quad (2.1)$$

Where: V_o = Free volume

A_o = Screw element open area

L = Screw length

A_o can be calculated for each screw element by subtracting the screw area from the barrel area. This clearly indicates that the greater free volume available the greater the extruders throughput capacity. Also it can be seen that the free volume is directly related to the ratio of the screw elements outer diameter, D_o, and the screw elements inner diameter, D_i, and the shaft centreline distance. Figure 2.11 shows the defined outer and inner diameters and their effect on the centerline distance of the shafts.

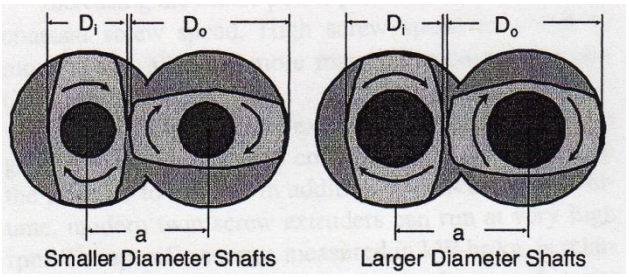


Figure 2.6 Indication of inner/outer element diameters and effect on shaft centerline[13]

This also has a direct consequence on the ability of the screw shafts to transfer the available motor torque to process the material in the extruder. With increasing extruder free volume, a high D_o/D_i value, more space is available to process material in the barrel due to deeper screw channels caused by a small value of D_i. With deeper channels the metal between the channel bottom and the screw shaft decreases and as a result provides less area to transfer the motor torque to each screw element. Conversely with less extruder free volume, a low D_o/D_i, there is little space to process material in the barrel but as a result there is a larger area to

transfer the motor torque to each screw element. But only a limited amount is needed since there is a reduced capacity for material in the barrel. Therefore a trade off is required between the amount of free volume and the torque required, needing to be carefully optimized. Figure 2.12 illustrates the relationship between torque and free volume as described by Giles et al [13].

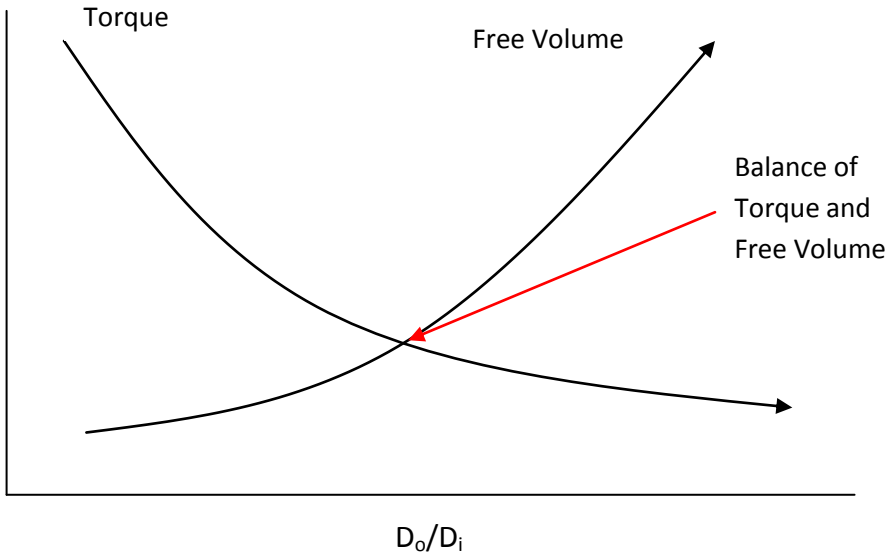


Figure 2.7 Relationship of torque and free volume relative to the ratio of outer/inner screw diameter.

A suggested guide for determining centreline distance, a, and flight depth, h, is given by Giles et al [13] in the form of the following equations.

$$a = \frac{D_o + D_i}{2} \tag{2.2}$$

$$h = \frac{D_o - D_i}{2} \tag{2.3}$$

Clearly industrial practice can overcome the problem of difficult dispersion via the usage of twin screw extrusion to apply the shear and elongational stresses and strains needed for effective distribution and dispersion of difficult formulations. There have been many studies into modelling these mixing processes in twin-screw extruders and the design of the various mixing elements. [29-37]. For example Cheng has made use of the FIDAP fluid dynamics analysis package to simulate the flow patterns of the polymer in the kneading discs region [29] and the conveying elements [30] of a ZSK-53 co-rotating twin screw extruder. This was done by introducing a tracer blob numerically and tracking the tracer particles as a function of location and time. Li had earlier conducted similar simulation studies on a counter-rotating twin screw extruder [32], simulating the flow patterns experienced. Lawal [31] conducted FEM (Finite element method) analysis on a co-rotating twin screw, using intensity of segregation distributions to characterize the mixing that occurred. Rauwendaal [35] [36] discusses the geometries and designs of mixing devices used in both co-rotating and counter-rotating twin screw extruders, as well as discussing the difficulties of dispersive mixing in single screw extruders and suggesting how new mixing devices could possibly improve their dispersive mixing capabilities to approach that of twin-screw extruders. Sernas [37] conducted flow visualizations on a Werner & Pfleiderer ZSK-30 co-rotating twin screw extruder, taking close up videos of the flow through a custom made window in the vent section of the extruder. A clear corn syrup was used as the extruded material and small quantities of sesame seeds used as tracers to visualize the velocity fields within the screw channels.

2.3 Scale down

Our research is concerned with developing a mini mixer capable of performing similar mixing processes but on a laboratory scale. Clearly all the concepts discussed above are important with regards to guiding the design of the screws. There is however, the problem that you need to have knowledge of how to scale down from known performing large twin-screw extruders to a smaller version. It is difficult enough to scale up from one and I briefly touched on the issues in chapter 1, but this case you're trying to do the reverse with the mini mixer and on a batch scale to ensure sufficient residence times. The HAAKE Minilab II Micro Compounder [5] is a commercial attempt to achieve this, comprising of an intermeshing co-rotating conical twin-screw system with the addition of a recirculation channel.

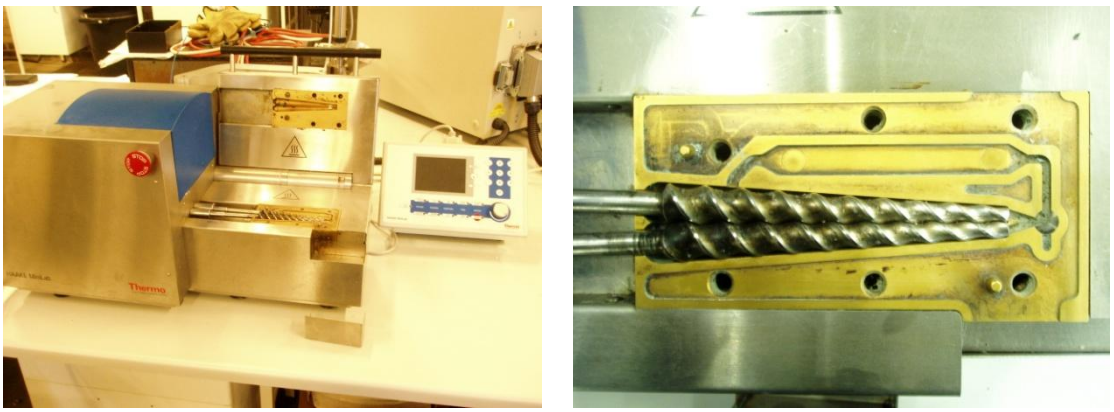


Figure 2.8 HAAKE Minilab II Micro Compounder at the university

More detailed specifications of this device can be found in Chapter 4. As touched on in Chapter 1 the design of a conical twin-screw is such that it has continued pressure generation down its length and that mixing is achieved by the profile of the screws kneading and shearing the material to achieve the mixing. This has obviously been done to reduce the need to design kneading blocks for the mixing processes and has

allowed them to create a machine that only requires 3g of material. Because of the size of the screws, only 109.5 mm in length, the re-circulation channel serves as a method to regulate residence time and for taking melt viscosity measurements. The weakness of this additional recirculation channel is that in this channel the polymer melt experiences a different history at the wall and at the center, which is something that does not occur normally in a twin-screw extruder. This machine produces only a very small quantity of material, so something a little larger is required. Hence the design proposed and discussed in Chapter 3. When looking at the practicalities of scaling down from a large extruder, it was necessary to keep in mind that the key section where mixing occurs in such a machine is where the specific mixing elements have been installed and that to some extent the design should revolve around this to meet the aims of the research.

A search through the patent literature to see if any similarly arranged equipment had been devised before found that the following three patents had been submitted previously.

The first patent is that of a *"Screw Press For Extruding PlasticMmaterials"*, submitted by Colombo [38] in 1961. This details an apparatus comprising of a multi screw design, ranging from 3 screws to 8 screws in a variety of configurations.

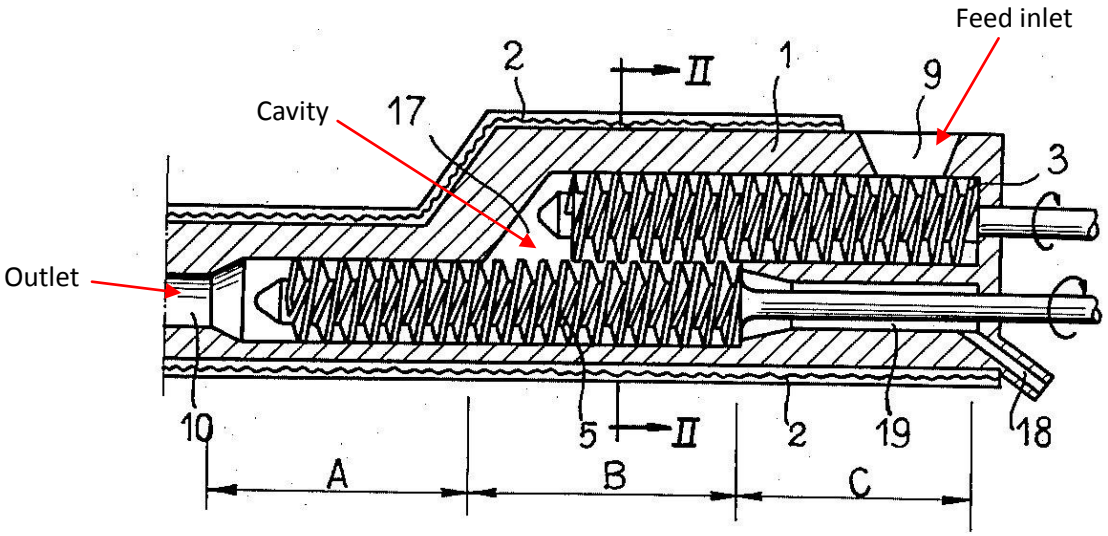


Figure 2.9 Longitudinal cross-sectional view [38]

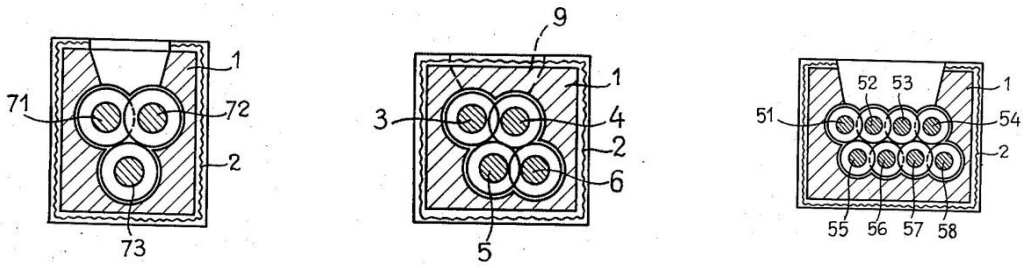


Figure 2.10 Cross-sectional depiction of screw arrangements [38]

Figures 2.9 and 2.10 illustrate some of the designs suggested in the patent to improve the homogeneity of the plastic materials being processed. The designs incorporate a feed inlet at the rear and an extrusion outlet at the front with a least a pair of parallel screws mounted inside the feed inlet. These screws rotate such that they carry material forwards with the screws engaged to compress and therefore break up, heat and intermix the plastic material fed to the machine. Positioned beneath the first set of screws, such that they over lap and form a small cavity as a region of decompression, is a second set of screws. The author suggests that this tiered arrangement discontinues compressive heating and reduces the possibility of overheating, and allows the venting of devolatile gasses and can be repeated until the die is reached. The tri screw cross-sectional arrangement depicted in figure B,

shows some similarities to the screw and rotor arrangement shown for the minimixer in Chapter 3.

The second patent is that of a *"Pasta Making Machine"* submitted by Mella [39] in 1981. This comprises of a kneading chamber positioned vertically above an extrusion chamber with an interconnecting passage between the two. Figure 2.11 shows the cross-sectional depictions of the machine proposed in the patent.

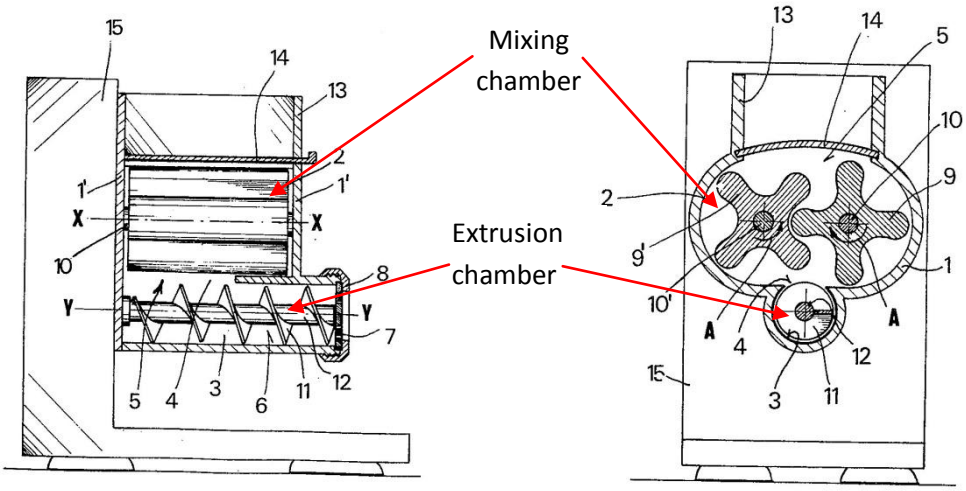


Figure 2.11 Cross-sectional depictions of the pasta making machine [39]

The device takes the form of a kneading chamber positioned above an extrusion chamber with an interconnecting opening between the two. The kneading chamber houses two intermeshing counter-rotating kneading devices mounted side by side. The extrusion chamber houses a simple Archimedean screw which is positioned below the two kneading devices. The shafts mounting the kneading devices and the screw are driven simultaneously by a geared motor. During the mixing operation the motor is driven such that the rotation of the Archimedean screw draws material away from the die area, thus constantly drawing the pasta dough back up into the mixing chamber. For discharge the rotation is reversed so that the Archimedean

screw draws the dough towards the extrusion die. As will be seen in Chapter 3, this operation of the pasta making machine is very similar to that of the mini mixer.

The third and final patent that was discovered was that of a *"Conching Machine with Multiple Rotors"* submitted by Braeker et al [40] in 1996 for the processing of chocolate pastes. Figures 2.12 and 2.13 depict the cross-sectional views of the conching machine.

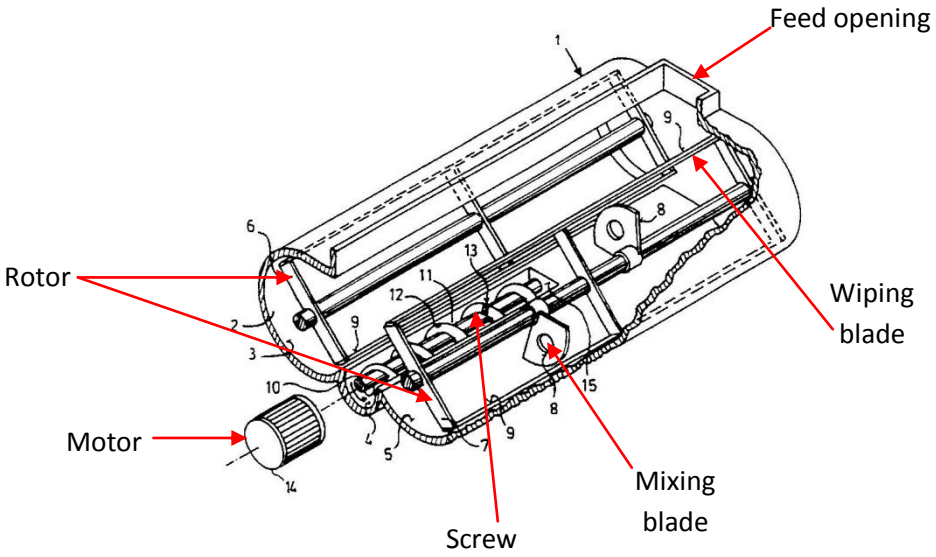


Figure 2.12 Longitudinal cross-sectional view of the Conching Machine [40]

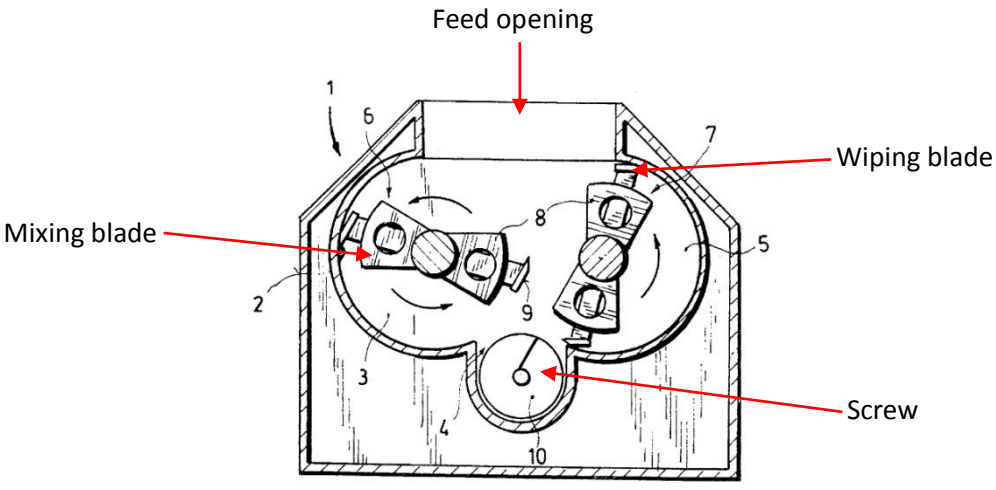


Figure 2.13 Cross-sectional view of the Conching Machine [40]

The machine comprises of a pair of co-rotating rotors aligned side by side within a figure eight mixing chamber, positioned above an Archimedean screw. The Rotors have wiping blades attached to sweep the walls of the mixing chamber of material and mixing blades to perform the actual mixing process of the paste. The screw is there to provide a kneading, compression and refining of the paste against the wall of the trough it is housed in. The machine as a feed opening that runs the length of the entire device and is positioned centrally above the mixing rotors.

These designs show a similar mixing cavity and shaft arrangement to that proposed in this research, so in some ways the idea to use this arrangement is not new but it has not been developed for an application with the emphasis of fitting it with kneading blocks that would be found typically in a twin screw extruder to create the conditions for dispersive mixing within polymer melts.

Chapter 3: CONCEPTION, DESIGN & BUILDING OF THE MINI-MIXER & RELATED EQUIPMENTS

3.1 Introduction

In the previous chapters, it has been emphasised that when viscous materials like polymer melts and soft solids are mixed with tiny amounts (~1%) of non-dispersed solid agglomerates such as pigments and other additives of micron and nano sizes the challenges of designing an appropriate mixer on a large or small scale are enormous. Turbulence cannot be achieved and the mixer must develop flows and stresses which disperse and distribute the additives components throughout the viscous mass. In the introductory chapter, it was explained that these mixers types are generally bulky, demand high power and perform their tasks using very narrow gaps with high shear and elongation rates and stresses. It was concluded that of all of the mixers available, the co-rotating twin screw compounding extruder is the machine most suited for such application. In this research this background information was used as a basis to develop a new laboratory or mini-mixer which is now presented. The experimental work is thus an **essential part of the achievement of this research.** It is not, as in other classical research, an established design which was being tested but a new design. The experimental work then becomes one of **conceiving, designing, building the mixer and testing it** in a variety of ways, including comparing its performance with other mixers, in order to demonstrate its unique ability: *that of replicating mixing that occurs in the larger twin-screw extruder, the machine of choice in industry.* It must be stated at the outset that this new design was proposed by my Supervisors, Professor Gale and Professor Benkreira

in the original application submitted to EPSRC. This was followed by the building of the prototype, again not on my instruction but on the instructions of my supervisors. Nevertheless, an essential objective of the work was to understand the rationale behind this new design in order to "own" it and used it appropriately in the research.

3.2 The Inspiration & Rationale Behind The New Design

The starting base and the inspiration for this new design must be the co-rotating twin screw extruder which performs well. The effectiveness of the co-rotating twin screw is due to its design which combines 3 elements: intermeshing screws, mixing cams and elements along an effective mixing length. Inevitably, this and other similarly designed machines require large quantities-kilogram size and larger of the materials to be processed and are not suitable for laboratory research and formulation work. Clearly, it would be desirable for research purpose as well as expediency, economy and health safety, especially when handling nano-additives, to develop laboratory equipment which operate at the gram scale and can replicate the intense mixing which occurs in the large machines used for production. This is precisely the aim of this research as explained in the Introduction. Such mini-mixers would be very useful as a research tool for studying dispersive mixing and its scale-up to larger machines and would give the opportunity to develop new products quickly and cheaply in the laboratory prior to production at the larger extruder scale.

A simple and logical solution would be a smaller version of the co-rotating twin screw compounding extruder, producing samples which are similar to production materials and in a form suitable for testing. However, to duplicate mixing in the larger scales, these small machines must be relatively large in size (long) and would

need significant amounts of material to fill the barrel, between runs. The miniature versions developed by instrument companies and academic research groups, which combine twin screw extrusion mixing with batch mixing using a re-circulating channel (see Figure 3.1) do not replicate the actual flow conditions. This is because in the re-circulating channel, viscous fluids such as molten thermoplastic will experience very low velocity shear at the channel surface so that this material experiences very little exposure to the screw mixing and may stagnate and thermally degrade. Also, the material remaining in the channel when mixing has been completed will require manual removal.

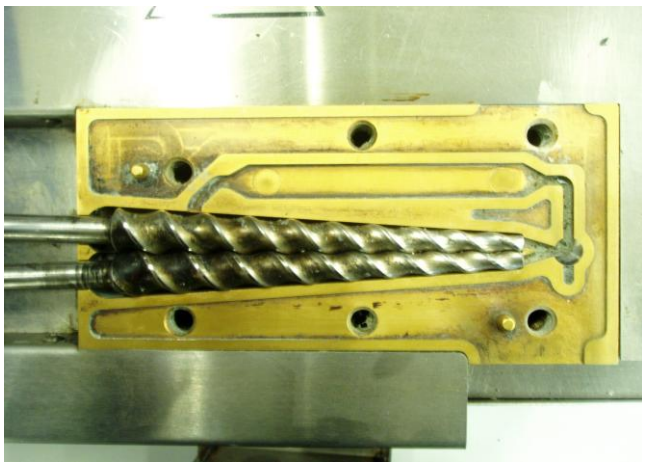


Figure 3.1: Haake Rheomex CTW5

In the new design used here the need for a recirculation channel was circumvented by incorporating a third screw positioned axially and perpendicular with the mixing elements of the co-rotating intermeshing twin screw. Axial movement of the material required for uniformity of mixing is thus achieved. This simple but effective mean of re-circulating the material is at the heart of this new design. It then enables us to reduce the size of the whole apparatus down to a very small device holding typically 10 to 40g of material, whilst as explained later retaining the ability to

discharge the mixed material as one or more strands or as a strip for testing. This device then becomes a "ready made" research tool not only to develop new products, nano-composites included, but also develop further our understanding of dispersive mixing and experiment with new mixing geometries leading to new more effective designs.

3.3 The Supporting Methodology Of The New Design

The conception of the minimixer was based on a series of inventive steps followed by the building of a working prototype, its successful testing, a comparison of its performance against performance obtained with currently available laboratory instruments and full scale equipment, a flow underpinning of how this new device functions and finally an extension of the original concept to other new designs. The key steps leading to the design are described below.

Methodology Step 1- Critical Appraisal of Current Technology: This is an essential step that informed and guided the design work by my Supervisors. As explained in Section 1, the shortcoming of a mini version of the large machines is that to allow sufficient mixing time, they must circulate the once mixed material back into the extruder. The re-circulating channel – a piping loop- cannot replicate the actual flow conditions in a full scale machine. Viscous fluids such as molten thermoplastics will experience very low velocity at the channel surface so that the material may experience very little exposure to the screw mixing and may even stagnate and

thermally degrade. Thus a new step-change in the design was required to ensure recirculation without an external loop.

Methodology Step 2- Adding the Inventive Step: In the new design (see Fig. 3.2), the mixing achieved in large co-rotating twin screw compounding extruders is reproduced by using the same type of rotors and optionally screw segments in a similar figure-of-eight barrel but add to it-**and there is the inventive step**- a third rotating screw mounted below the two sets of rotor in a triangular formation; the screw acting as a feeder screw and combining with the elements to achieve the mixing that is achieved in a compounding extruder. When this two cam/screw system is housed within an enclosure fed at one end of the barrel and then closed, it operates as a small batch mixer continuously mixing and re-circulating the material between the cams and screw. Mixing time can thus be controlled infinitely and this enables us to reduce the size of the whole apparatus down to a very small device holding typically 10 to 40g of material i.e a bench top mixer. To discharge the batch, it is a simple matter of reversing the rotation of the screw and if the barrel is fitted with a die, the mixed material can be discharged as one or more strands or as a strip for testing. Clearly the design is flexible and with a modular construction and guided by advances reported in the literature, a range of alternative designs could be tested, for the screw and mixing cams, to arrive at an optimized design:

- Mixing elements can be in the form of two lobe, three lobe, or multiple lobe cams, cylinders with eccentric centres or any combination which provides good dispersive mixing. Cam type elements can be positioned at right angles

to adjoining pairs or mounted at successive smaller angles to form an overall screw type conveying pitch as used in twin screw compounding extruders. The widths may also be varied provided the paired elements are of the same width.

- The degree of intermesh of the mixing elements and screw segments will depend on the distance between the centre lines of the figure-of-eight chambers.
- Twin screw segments can be added e.g. for longer mixer lengths, in order to increase axial movement of material.
- The (single) screw may rotate in the same or opposite direction to the mixing elements, but co-rotation is preferred as this increases drag flow and hence screw conveying efficiency.
- The (single) screw may rotate at a faster, equal or slower speed than the rotors.
- The (single) screw can have a channel section typical of the type used in single screw extruders, but to optimise pellet conveying during mixer filling and melt conveying with screw rotation reversed during emptying, the screw channel depth may be varied across its width and its flank radius optimised for pellet conveying in one direction and melt conveying in the opposite direction.
- The length of the mixer can be increased or decreased to change its mixing capacity by adding extra barrel, mixing and single screw segments.

Methodology Step 3- Designing and Building a Prototype: Following the initial conception and optimised design, the research then proceeded to the building of a prototype by an external contractor using a modular construction which gave the flexibility later in the programme to experiment with the al ternatives listed above. Except for the screws and the mixing elements which were made from steel grade EN40, most of the remaining parts were in steel grade EN24. The prototypes will now be described with reference to the accompanying drawings. To gauge the scale of the equipment, it is helpful to note that in Figure 2 below, the single screw diameter is 19mm, the barrel is 75mm in diameter and the overall length is 100mm. Therefore in comparison to standard extruders the L/D is low (about 5) but here because of the recirculation mode a larger ratio is not necessary. As for flow rate, typically (this was properly calibrated, see section 3.4.2) the cumulative discharge from the mini-mixer would vary from 18 to 19 grams in a 20 gram charge.

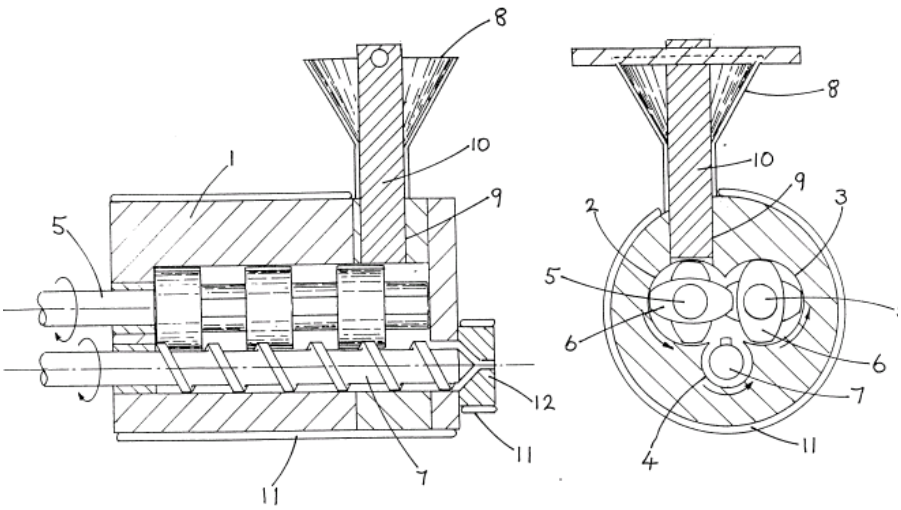


Figure 3.2 Prototype Minimixer Barrel

Figure 3.2 shows the mixer which consists of a barrel (1) having three parallel cylindrical chambers (2) (3) and (4) in which the axes of cylindrical chambers (2) and (3) are positioned at a distance less than their diameter and cylindrical chamber (4) is tangential to cylindrical chambers (2) and (3). Within each cylindrical chamber (2) and (3) are positioned shafts (5) upon which fit mixing elements (6) with geometries as used in twin screw compounders or screws as used in twin screw compounders, or a combination of the two. A conveying screw (7) is positioned within the tangential cylindrical chamber (4). Material enters the mixer through the hopper (8) and down the chute (10) which is closed during mixing. The barrel (1) is heated by heating elements (11) and the temperature controlled by a controller via a thermocouple. Shafts (5) are arranged to rotate at the same speed and in the same direction. The screw (7) rotates in the same direction as the 2 shafts (5). In the embodiment shown in figure 3.2, emptying is by reversing the rotational direction of the screw (7) so that the screw pumps the mixed material out of the mixer via the shaping die (12). The die (12) is of a form to provide the required shaped extrusion for testing. Figure 3.3 shows an alternative arrangement in which the screw (7) is nominally the same length as the mixing chambers (2) and (3) and the screw chamber (4) is terminated with a valve (13) which is opened to allow discharge of material when mixing is complete without reversal of the direction of the screw (7). For this arrangement the hopper (8) and feed pipe (9) are positioned at the opposite end to the valve (13) and die (12). Figure 3.4 shows an arrangement in which the single screw (7) in Figure 3.2 is replaced by two intermeshing screws (14) to provide more positive pumping and complete emptying of the mixer. In all these arrangements, the mixer drive can be connected to the mixer with a torque

measuring device which continually records the torque provided by the drive motor so that technical data on the mixing process can be obtained.

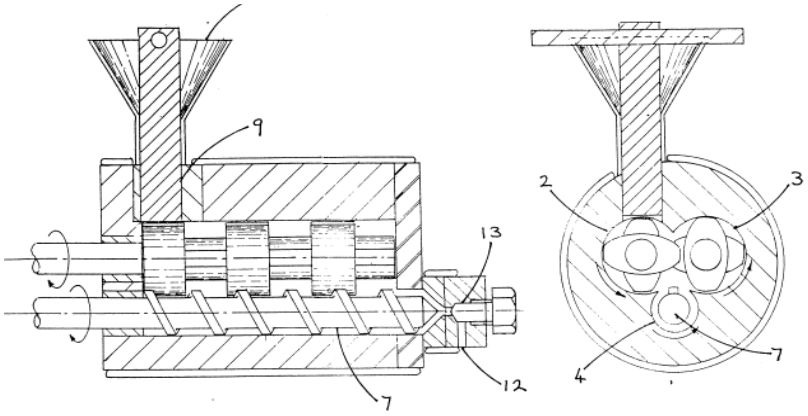


Figure 3.3 Alternative design with rear feed and valve

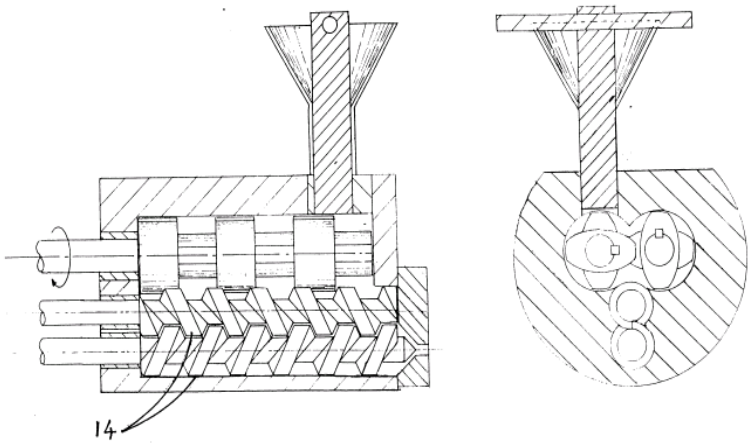


Figure 3.4 Alternative design with twin-screw arrangement

3.4 THE PROTOTYPE MINIMIXER

3.4.1 The Minimixer Design

Having described the various design elements of this new minimixer, we now present the details of the prototype. It is essentially the basic design as described in relation to Figure 3.2 above.

The main drive for the mixer is provided by a three phase 0.55 kW right angle geared motor. Power to the geared motor is via a Eurotherm 650 single to three phase frequency controlled inverter. The output from the geared motor is fed into a splitter gearbox which provides three output shafts to drive the mixer screw and cam shafts. The splitter gearbox consists of an internal gear which drives the screw. The cam shafts are driven by two spur gears mounted within the internal gear see Figures 3.5. The gear ratios of the internal gear and the spur gears are such that the speed ratio of the screw speed to mixing shaft (cam) speed is 1 to 3.5 i.e the cams run at 3.5 times the screw speed. Also, the splitter gearbox arrangement is such that the three output shafts rotate in the same direction i.e co-rotating in both the mixing and discharge modes.

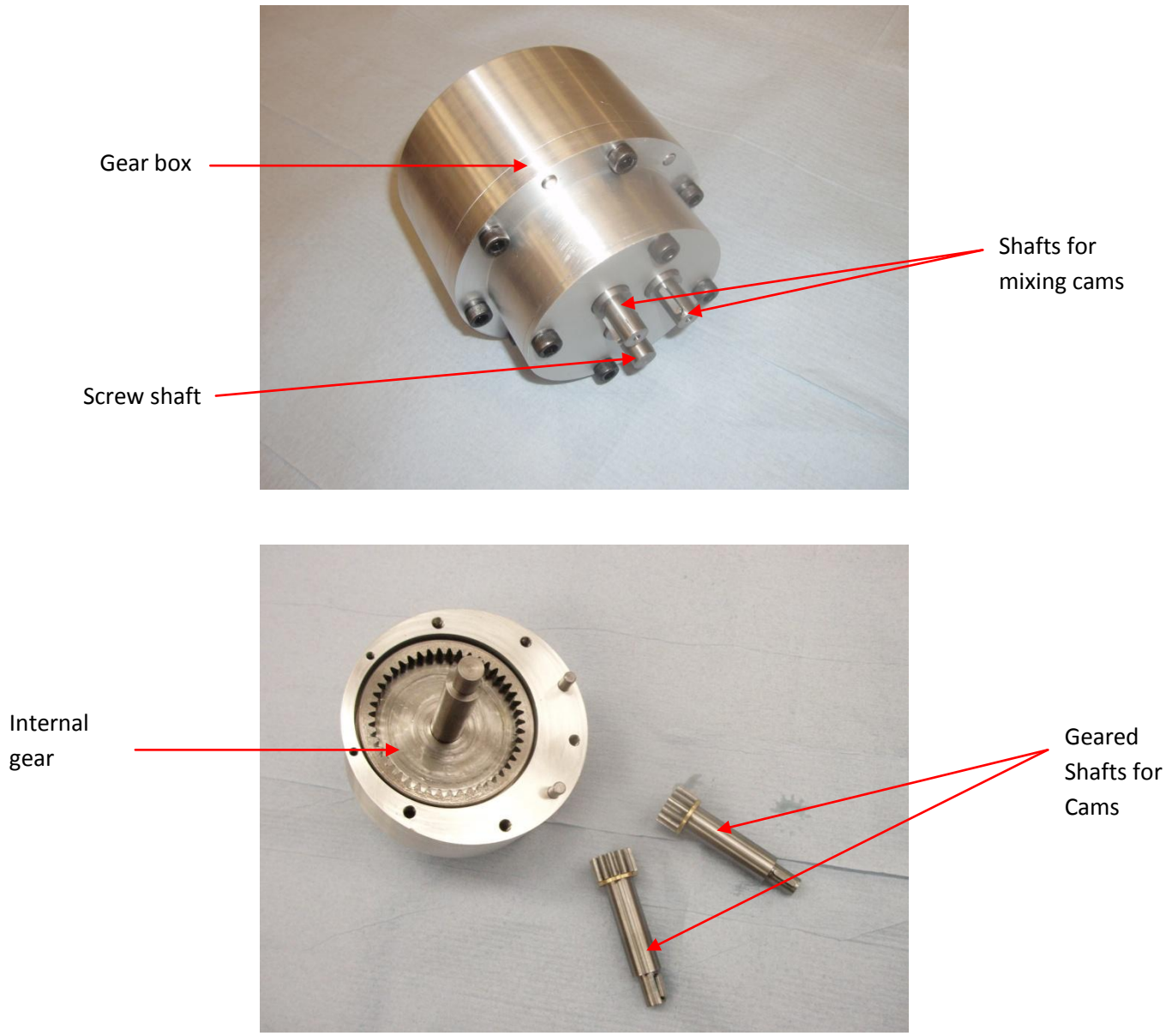


Figure 3.5 Details of mixer gearbox

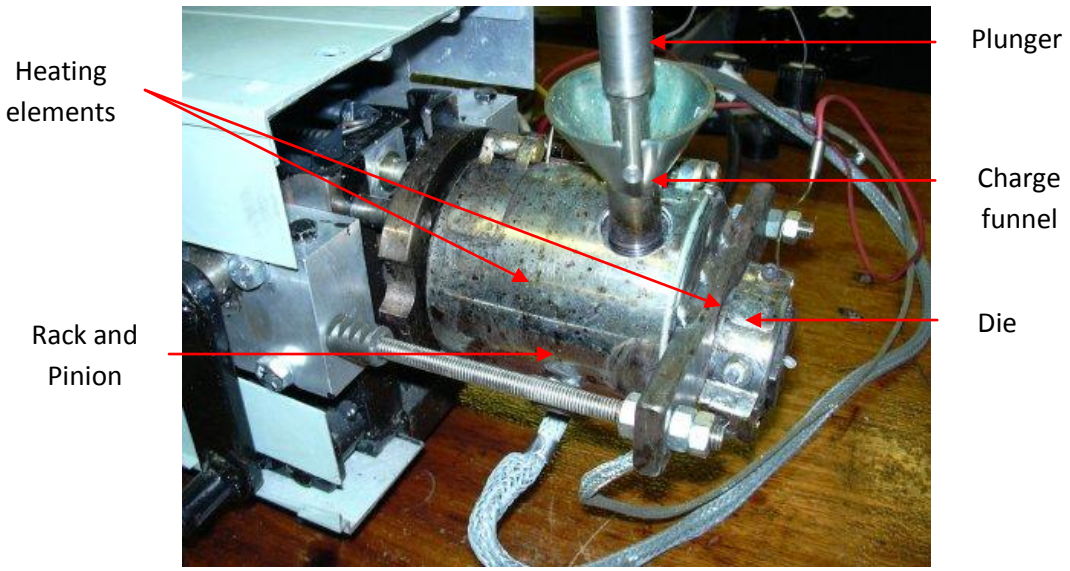


Figure 3.6 Details of mixer body

The main barrel of the mixer comprises of a solid cylinder that has had three channels bored out of the centre to form a cavity to house the screw and mixing elements. This main barrel is only 95 mm in length and is held in place using a rack and pinion system. The back part of the barrel is slightly indented so that it slots firmly into the back plate of the mixer to form a tight seal when closed. At the end of the screw a 3mm diameter die is affixed to the face plate to enable material to be discharged as a strand.

There are two types of mixing element used within the mixer. The first type of element (paddle shape) is designed to sweep the charged material down into the screw, and is installed in two pairs beneath the charge funnel of the mixer. The second type of element takes the form of off centre circular cams, which are installed in four pairs. Their arrangements are shown in figure 3.6. The elements are designed to be self wiping and are affixed in place using grub screws.

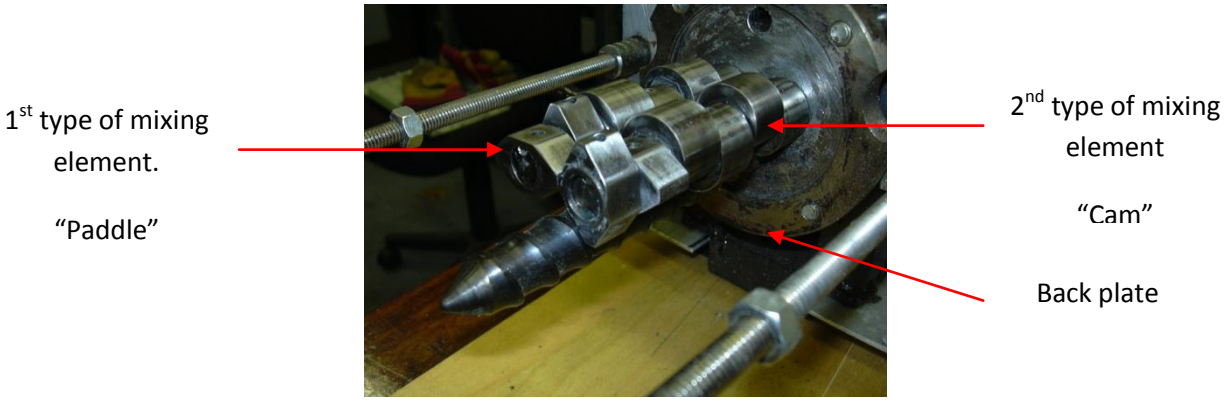


Figure 3.7 Details of mixing elements

The inverter drive which supplies the power to the geared motor is housed in the main control box which also houses the temperature controllers and the read out of the motor speed (see figure 3.7). The mixer barrel temperature is controlled by zone 1, while Zone 2 refers to the temperature control of the die. CAL 3300 series temperature controllers are used with thermocouples housed in the die and the mixer barrel and control the power to the electrical heating elements, using ambient room temperature for cooling.

A part cross section diagram of the prototype mixer can be seen in figure 3.8 together with a list of the relevant parts.

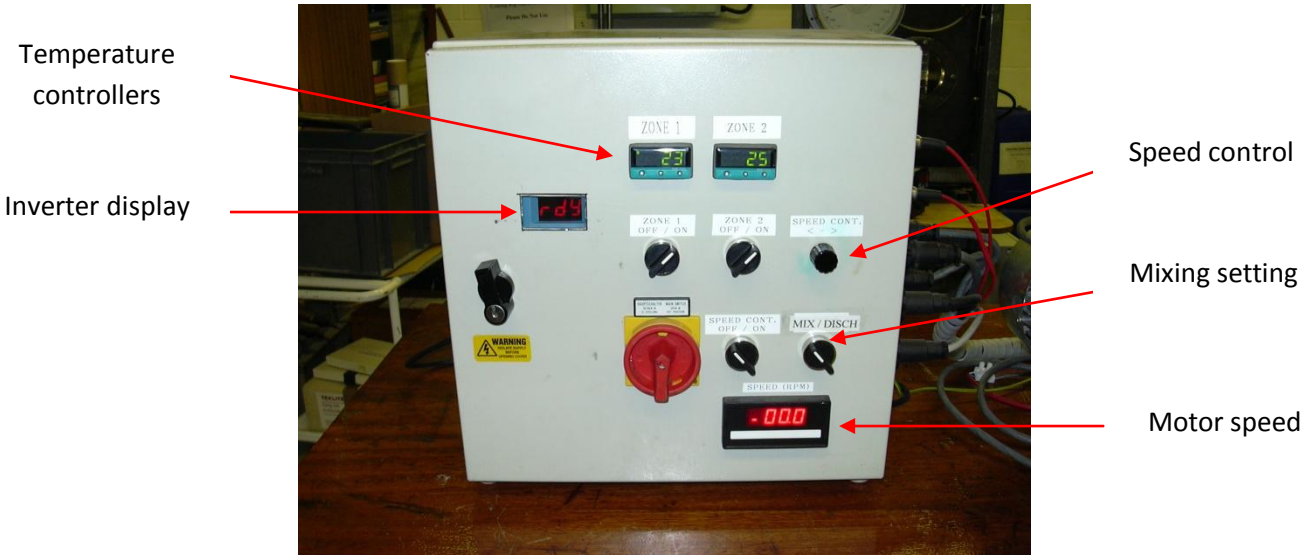


Figure 3.8 Mixer control box

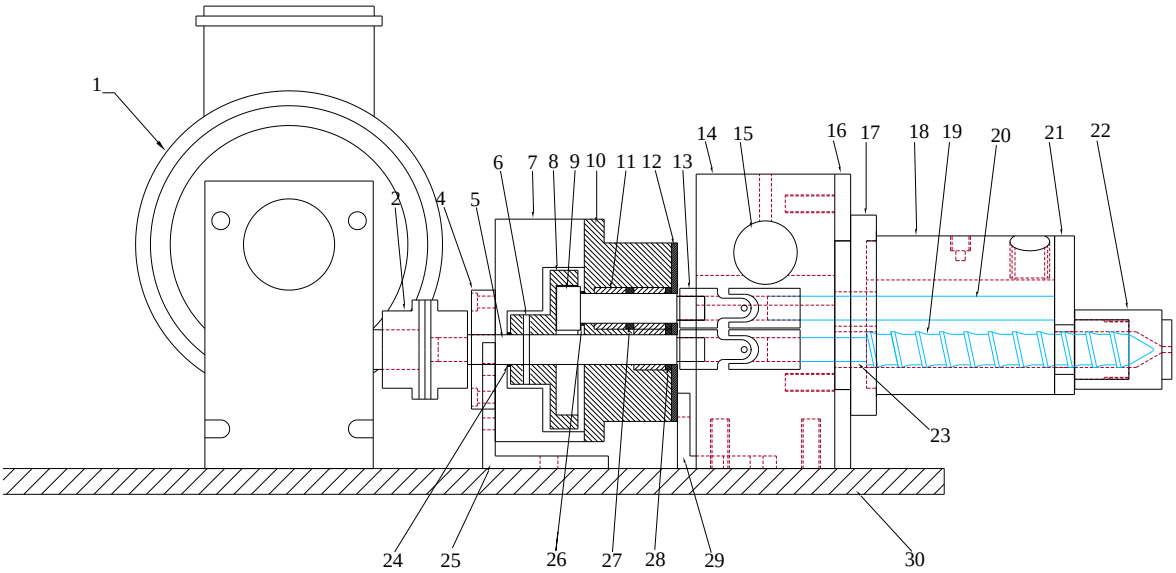


Figure 3.9 Schematic of the prototype minimixer

Table 3.1 Parts list for the prototype minimixer

Item	Description	Item	Description
1	0.55 kw Geared Motor	17	Barrel Locating Plate
2	Flexible Coupling	18	Main Barrel
4	Bearing Round Type	19	Screw
5	Main Gear Shaft	20	Cams shaft (cams and paddles not shown)
6	Pin	21	Barrel End Plate
7	Aluminium Gearbox Housing	22	Extrusion Die
8	Internal Gear	23	Oilite Bushes
9	Pinion Shaft	24	Bronze Washer
10	Aluminium Gearbox Housing	25	Gearbox Mounting Bracket
11	Needle Bearings	26	Brass Spacers/Washers
12	Gearbox Cover Plate	27	Brass Spacer
13	Universal Joint	28	Brass Spacer
14	Rack & Pinion Housing Block	29	Gearbox Mounting Bracket
15	Spur Gear	30	Base Plate
16	Barrel Mounting Plate		

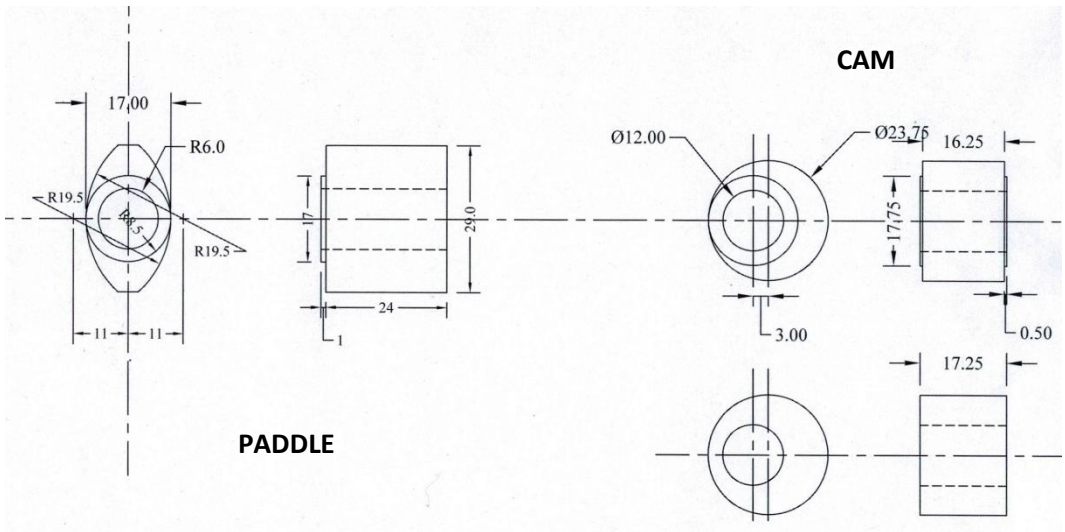


Figure 3.10 Details of mixing cams and paddles

3.4.2 Minimixer Calibration Data

Gearbox speed data.

Firstly it was necessary to check the ratio of the gear box so that speed at which the mixing cams and paddles were rotating at could be determined. The readout on the mixers control panel reads in RPM and corresponds to speed of the screw. A tachometer was used to verify this and check the speeds of the cams. The details can be found in Table 3.2 and presented in chart 3.1

Table 3.2 Mixer Gearbox speed data

Read Out (RPM)	Screw Speed (RPM)	Cam Speed (RPM)	Ratio of Cam to Screw speed
20	20	69.0	3.45
25	25	87.0	3.48
30	30	103.7	3.45
40	40	138.0	3.45
50	50	173.0	3.46

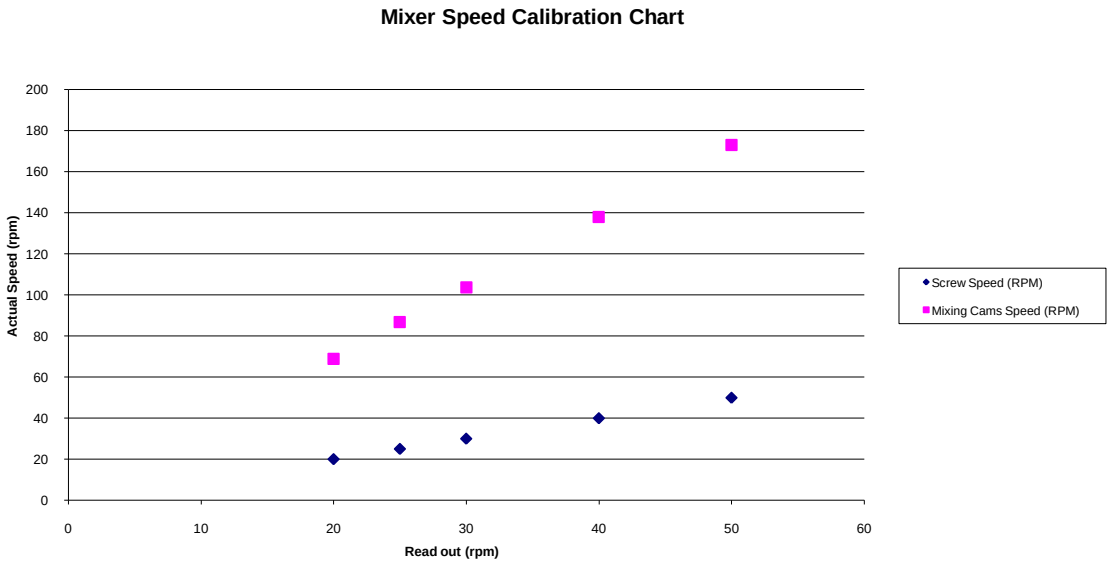


Chart 3.1 Mixer Speed Calibration Chart

Cumulative discharge data

A check on the cumulative discharge of the mixer was performed and the details of this can be found in table 3.3 and presented in chart 3.2

Table 3.3 Cumulative discharge data

	Discharge time (minutes)	Mass collected (g)	Cumulative mass (g)
Run 1	1	3.4113	3.4113
	2	5.0712	8.4825
	3	3.2766	11.7591
	4	1.6711	13.4302
	6	1.6211	15.0513
	10	1.8626	16.9139
	14	0.8837	17.7976
Run 2	1	3.8223	3.8223
	2	5.4116	9.2339
	3	3.3768	12.6107
	4	1.7740	14.3847
	6	1.9330	16.3177
	10	1.8556	18.1733
	14	1.1750	19.3483
Run 3	1	3.4103	3.4103
	2	5.3446	8.7549
	3	3.7551	12.5100
	4	1.8979	14.4079
	6	1.8500	16.2579
	10	1.7467	18.0046
	14	0.8536	18.8582

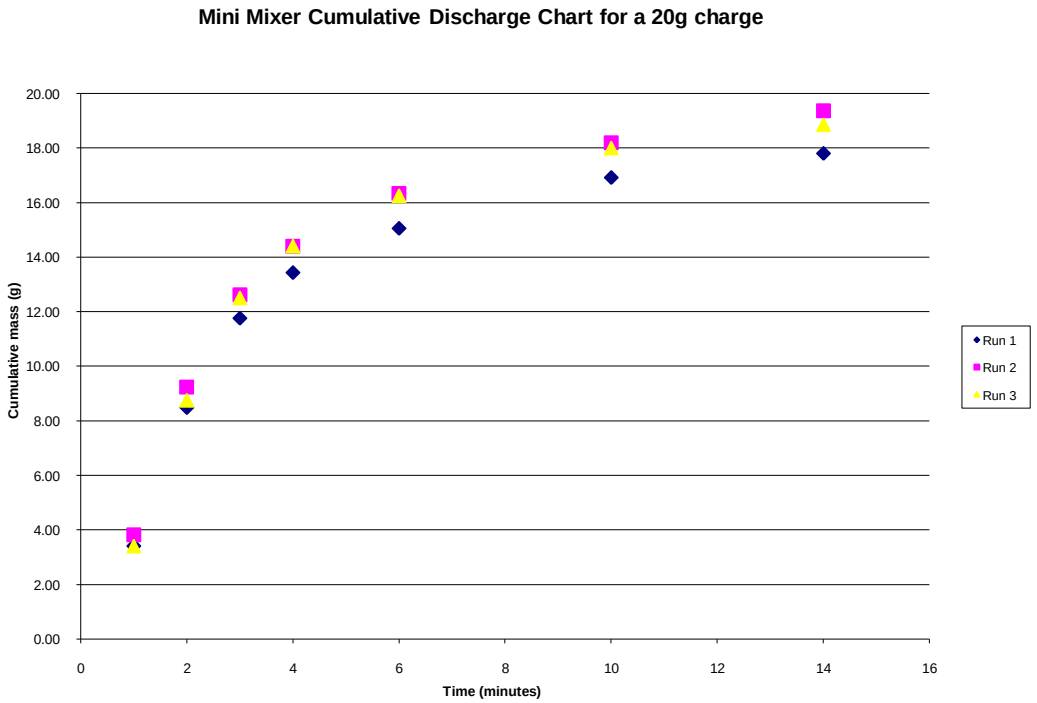


Chart 3.2 Mini Mixer Cumulative Discharge Chart

3.5 Associated Equipment: The Mini-Extruder & Blown Film Line

3.5.1 Introduction

Having conceived, designed and built the minimixer, it became apparent early during the course of the research project as conceived by my Supervisors that it would be desirable to provide a complementary laboratory equipment to evaluate mixing in an actual polymer processing operation. For this purpose, a mini extruder was designed and built to provide a machine capable of creating blown films on a small scale for analysis under the microscope for the agglomerates present in masterbatches produced within the mini mixer. Such a machine and its successful production of well mixed films would underpin strongly the credibility of the minimixer. Only a limited number of trials were carried out in this device as blown films with additives were provided by a collaborating company (Colloids Ltd, see section 4.3.1). This equipment is included here for completeness to direct future research when blown film are required in house and alongside the masterbatch produced with the minimixer. It will form indeed a major recommendation for future work.

3.5.2 Design & Building of the Line

The design and manufacture of this line did not require major ingenuity as the intention was not for the single screw extruder to perform extra-ordinarily from a mixing perspective. Indeed it cannot in any case. The line was thus essentially a single screw extruder fitted with a blown film die. The extruder was to be fed masterbatches produced by the minimixer, so the performance of the extruder was to melt-pump and ensure good distributive mixing of an already assumed very well or not dispersed masterbatch as produced by the minimixer

under various operating conditions. This line was thus an evaluator of the minimixer performance. However in order to ensure good mixing, a mixing head of the cavity transfer (CTM) or peg modes was added to the single extruder. The mini extruder was thus a single screw extruder mounted on an aluminium frame, with two modular sections towards the end of the main barrel. The first modular section allows either the installation of peg mixer or a cavity transfer mixer. The second modular section comprises of the blown film die, but this can be replaced with another die if required. Therefore, this associated line can be extended to assess mixing as occurring in the mini-mixer in other polymer processing conditions (sheets, tubes, etc.). Given below are further specifications and corresponding drawings and illustrations of this mini-extruder and blown film line. All these specifications were undertaken by my Supervisors as part of the bigger project contracted to EPSRC. A full understanding was however required to enable me to process the mixing experiments.

The screw running the length of the extruder has a diameter of 20 mm and an L:D ratio of 19.5:1 (see Figure 3.10) and this conforms to classical design. There are also two ports just before the mixing section for the installation of pressure-thermal transducers.

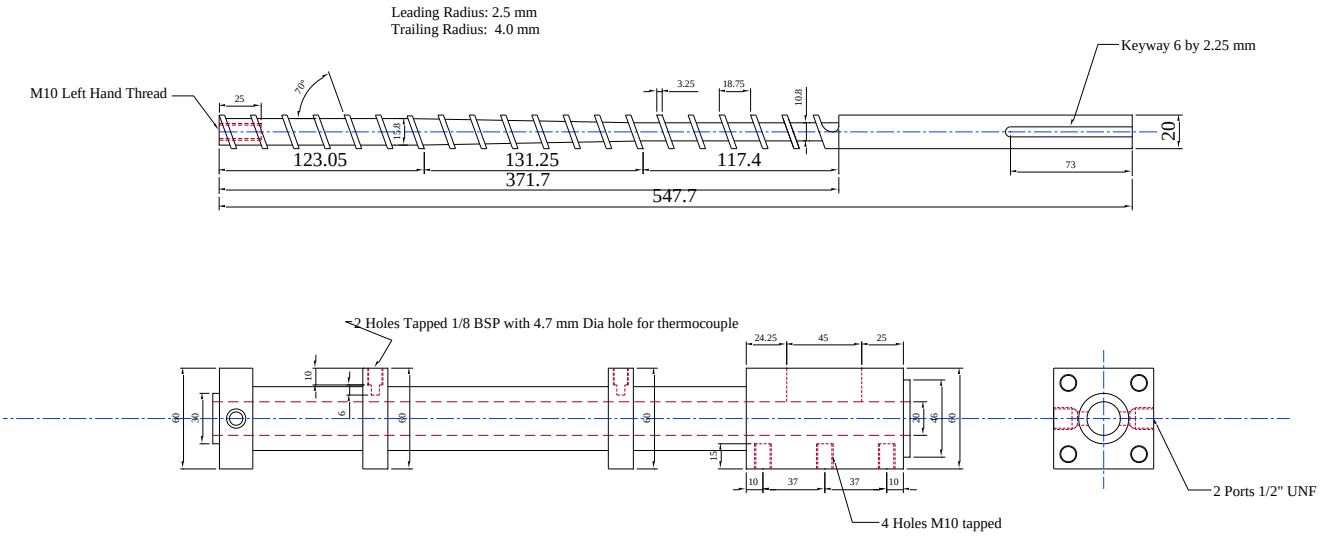


Figure 3.11 Details of the screw and barrel for the blown film machine.

Figure 3.12 Miniature Cavity Transfer Mixer (CTM)

The drive for the screw is a 0.37 kW motor which is powered by an inverter in the main control panel. A gravity fed hopper is used to keep the metering section of the screw constantly full of pellets.

The blown film die is an annular die in which air can be introduced down through the centre to inflate a bubble of polymer. Around the outside of the die an air ring is attached which forces air in a radial fashion around the outside of the formed polymer bubble, creating a

vortex of cool air. The resultant bubble is nipped by the take up rollers directly under the die. These rollers maintain the seal at the base of the bubble as the film is hauled off onto a self winding roller. The motor for the haul off system is only 0.08 kW; this is a safety feature in case something unwanted becomes trapped between the rollers, causing them to stop rotating instantly. The rollers are arranged such that it is self winding, with the take up roller free to move as the diameter increases with more film being collected.

The size of the bubble formed was determined by a number of factors: -

- The throughput of polymer along the screw.
- The amount of air used to inflate the bubble.
- The flowrate of air from the radial die to cool the bubble
- The speed of the haul off drive.

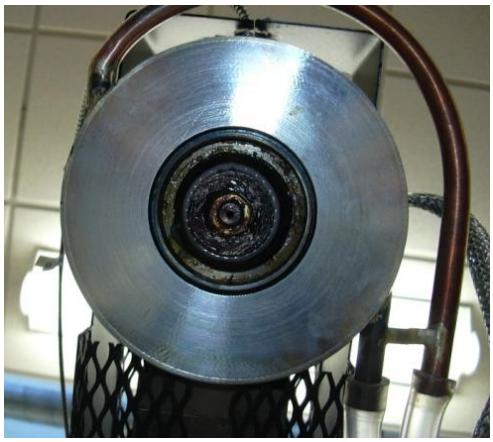


Figure 3.13 Blown film annular die

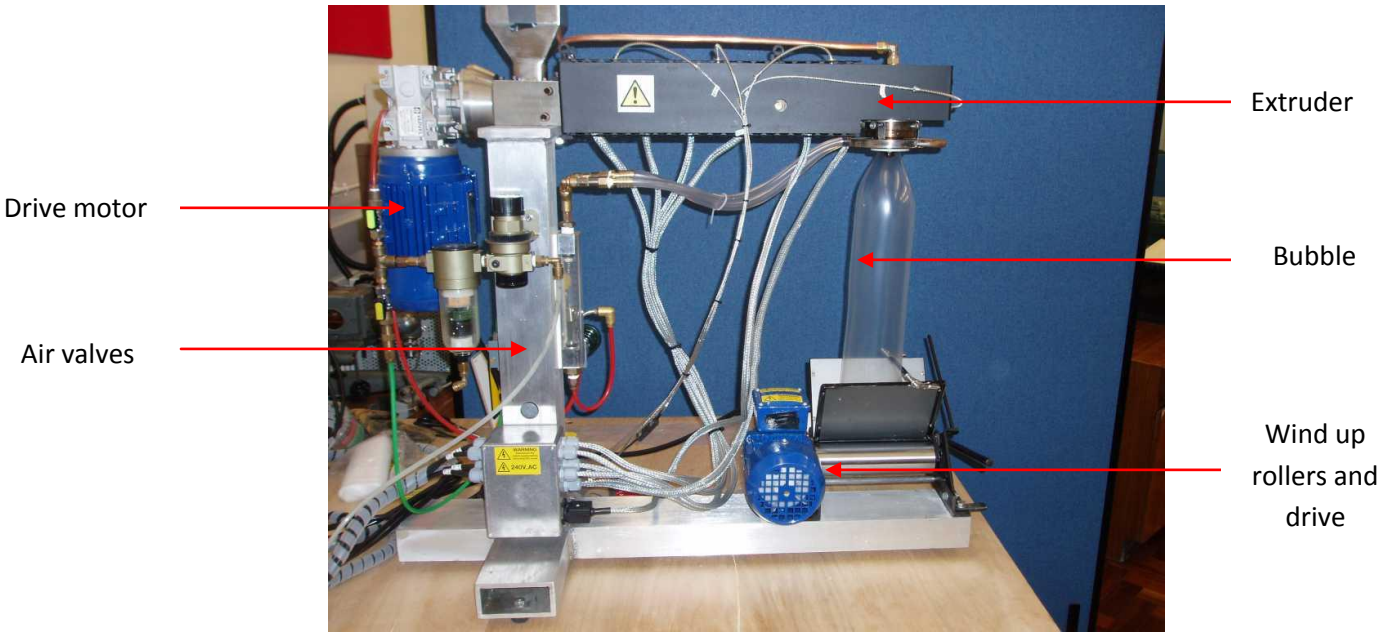


Figure 3.14 Mini extruder & Blown film.

3.6 Conclusions

We have in this chapter described the essential equipment of this research, a new mini-mixer, and an associated mini-extruder and blown film line. The conception and design of this mini-mixer was guided by the classical co-rotating twin screw, the work horse of modern compounding technology. The unique feature of the new design is not only its ability to replicate the intensive mixing which is observed in the large machine (it is essentially a similar design with paddles and cams carrying out the elongation high stress mixing) but it does so in a re-circulating manner thanks to the third screw positioned in between the adjacent co-rotating pair of screws. The inclusion of this third screw is the inventive step of this design. This research claims that this new mini-mixer will operate at the gram scale and can replicate the intense mixing which occurs in the large machines used for production. This new mini-mixer can thus be considered as a very useful research tool

for studying dispersive mixing and its scale-up to larger machines and that it would give the opportunity to develop new products quickly and cheaply at the laboratory prior to production at the larger extruder scale. Having presented the design and build of this new equipment, we present in the next chapter an experimental assessment of its performance.

Chapter 4: EXPERIMENTAL EVALUATION OF THE MINI-MIXER

4.1 Introduction

In the previous chapter, we introduced the design methodology that led to the construction of the mini-mixer and our expectations of its performance. The main and ambitious claim is that this mini-mixer will not only perform well on the laboratory scale but also it is capable of replicating mixing that occurs in standard extrusion machine at scale comparable to industry. A comparative evaluation with other mixers then becomes necessary. This was carried out and the results are presented here. First, however, an assessment of the mini-mixer with a range of additives, including additives known in the industry to be difficult to disperse had to be undertaken and we describe here the results of this key evaluation under the title of "Proof of Concept Mixing Experiments". Another important point we need to address in this evaluation is checking our claim that the three screw arrangements we have devised is able to induce re-circulation within the mini-mixer. This formed indeed the beginning of our evaluation exercise.

4.2 FLOW PATH THROUGH THE MINI-MIXER

Although the flow pattern in twin screw extruders is well established in relation to the degree of intermeshing, we needed in our prototype to provide the evidence of continuous mixing flow and recirculation between the three screws, the single screw acting as the feeder and the means of recirculation. To test this we fashioned a Perspex barrel for the

mini-mixer so that the mixing cams were visible during operation as shown in Figure 4.1 and observed the flow of a cold viscous fluid (honey). Air bubbles where used as an initial tracer to observe the flow pattern which was recorded with a video camera (Supporting videos can be found on CD).

The die of the mixer was initially blocked with a piece of tape while the honey was poured down the charge chute. The mixer was filled until there was a small air pocket visible at the top of the barrel. The speed of the mixing screw and cams was slowly increased, which is clearly shown in the videos. The movement of the air bubbles visible inside the mixer clearly show how material is pushed against the wall of the barrel and over into path of the pairs of mixing cams either side. As the speed of the cams increased the size of the bubbles reduced until at very high speeds the honey inside became a frothy liquid. Upon discharge, the videos clearly show how the screw draws the fluid towards the die while the mixing cams continue to sweep material around the barrel for additional mixing. The honey expelled from the mixer was found to be frothy and watery in consistency.

Figure 4.1 Mixer fitted with Perspex Barrel

The following observations were made from the visualisation experiments.

- That the screw did in fact draw material back towards the back plate to recirculate the contents.
- That screw successfully discharged the material through the die.
- That material flowed around the kneading blocks but was also drawn through the gap between the block and the barrel wall for dispersive mixing as described in chapter 2.
- That even in discharge mode, due to the kneading blocks being self wiping, some material would be swept up into the upper cavity for additional mixing. But because of the arrangement of the blocks, there was sufficient free volume for the liquid to drop down and keep the screw channel filled for discharge.
- That the dispersive mixing resulting from the kneading blocks was sufficient to reduce the honey to a frothy liquid that was almost water like in consistency.

Having ascertained that the re-circulation was full and effective as we had designed it to be, we can offer a mechanism of how the mini-mixer will operate with polymer melts. This is as follows and is illustrated in Figure 4.2.

- As material is fed into the barrel, the first four sets of elliptical cams break the bulk material as it is melting. The material falls down and is forced into the screw. As more material is fed in, the screw channels start to fill up and the clockwise rotation of the screw forces the melt towards the back of the barrel. As it is being pushed back, some of the molten material will be picked up by the circular self wiping cams. The circular cams shear some of the material against the barrel wall. The remaining material will be pushed sideways onto the adjacent cams.

- When sufficient material is fed into the barrel, the screw channels are completely full and the further addition of material forces it to cluster at the back plate. Here it is forced upwards onto the circular cams. These cams shear the material as described earlier and the material is forced towards the front of the barrel.
- The whole cycle then repeats. During discharge the screw rotates in an anti-clockwise rotation and pumps the material out through the die as a strand, while the cams continue to mix in the same fashion as described above until the barrel is empty and only the screw channel holds material.

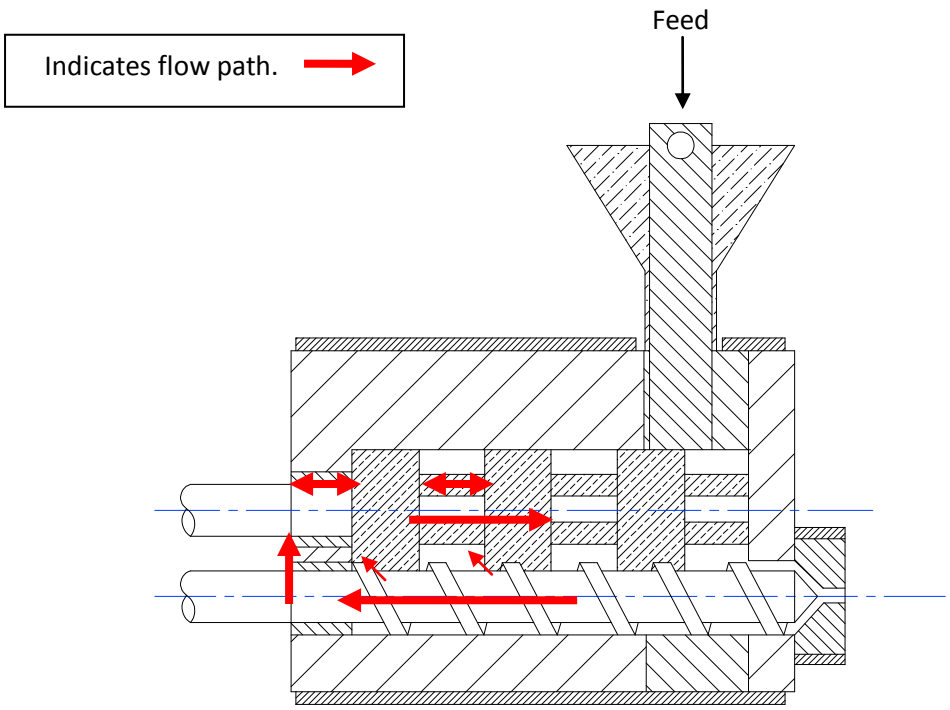


Figure 4.2 Diagram of flow pattern through the mixer during mixing operation.

4.3 INDUSTRIAL CASE STUDY EXPERIMENTS

In this part of the programme a series of industrial based case studies were performed to measure the extent of mixing that could be achieved with the mini-mixer. The first two case studies were "Proof of Concept" experiments, to determine that mixing was occurring. Once this was established we then proceeded onto the comparative measurements with other contenders- a laboratory instrument currently available and larger scale twin screw machines. These experiments were performed using (i) a colour masterbatch formulation currently used in industry (ii) an additive known to be difficult to disperse in polymers and (iii) conductive carbon black. Whereas in the first two cases we measured mixing directly, i.e. by observing a sample under a microscope and taking the corresponding mixing indices, with the carbon black, we measured mixing indirectly by measuring electrical conductivity as a function of carbon black loading and seeing what is the critical load, "percolation threshold" (as referred to in the introductory chapter), that produces conductivity and compare this with the other mixers. We have thus in this exercise approach the measurement in a number of complementary methods.

4.3.1 Mixing with Colour Additives

The colour additive was a phthalo green masterbatch recipe provided by Colloids Ltd. This masterbatch is produced by Colloids Ltd for use with injection moulding and blown film applications to provide a green pigmentation to a customer's products. It was recommended as an ideal material to begin initial trials with as, from their experience, it was known to suffer from agglomerates during production.

This trial was thus to investigate how well the mini mixer could produce a phthalo green masterbatch using the recipe provided by Colloids Ltd. This masterbatch would undergo testing for quality as performed by Colloids Ltd, in which the masterbatch would be mixed with fresh virgin polyethylene and passed through a blownfilm line at Colloids Ltd. Sample sections would then be cut from the resultant film and inspected under a microscope to determine if any agglomerates of pigment were present in the masterbatch. If they did, then they would show up as blobs or colour striations within the film. A film of the virgin polymer was also created to be compared against.

Table 4.1 details the recipe that was provided and the mass required for each component for the batch sizes considered. This recipe was then produced within the mini mixer under the mixing conditions and batch sizes shown in Table 4.2. The mixing conditions listed in Table 4.2 were decided on the basis that initial assessment indicated that 4-6 minutes and a speed of 30-40rpm were sufficient to produce good melting and mixing of a polymer. Thus conditions outside this range (whilst avoiding degradation as indicated by discoloration of a virgin polymer) were also taken as indicated in Table 4.2 to study the performance over a range of conditions. This same approach was used in the subsequent experiments described below. That is an initial mixing test was carried, learnt from and a range was then determined to assess performance in the range.

The recipe was measured out and premixed before being charged into the mixer. A consistent procedure was adopted and this was agreed in consultation with Colloids Ltd. The procedure was as follows:

1. All the materials bar titanium dioxide was to be first shaken together within a small polyethylene bag for 10 seconds.

2. The titanium dioxide was then added and the bag shaken for a further 10 seconds.
3. This mixture was then fed into the mini mixer.
4. Once charged, the mixing speed was set and held for the duration specified.
5. The resultant masterbatch was then discharged as a strand and collected.

Table 4.1: Phthalo Green Masterbatch Recipe

Component	**Composition (wt %)**	**Mass (g) required for batch**		
		15g	*20g*	*25g*
Phthalo Green (pigment)	30	4.5	6.0	7.5
Titanium Dioxide (pigment)	10	1.5	2.0	2.5
Zinc Stearate	2	0.3	0.4	0.5
PE Wax	10	1.5	2.0	2.5
Powdered LLDPE	48	7.2	9.6	12.0

- Phthalo green pigment that has a composition that ranges from $C_{32}H_3Cl_{13}CuN_8$ to $C_{32}HCl_{15}CuN_8$ depending upon desired colour. This colour ranges from a bright to a dark bluish green.
- Titanium Dioxide (TiO2) is used typically as a white pigment or in the case of this masterbatch, its use is to determine the resultant shade of green observed.
- Zinc Stearate ($Zn(C_{18}H_{35}O_2)_2$) is a zinc soap that repels water and is used as a releasing agent and lubricant.
- PE Wax is used as an additional releasing agent and lubricant for the masterbatch.
- Powdered Linear low density polyethylene (LLDPE) is the bulk polymer for this masterbatch.

Table 4.2: Conditions in mini mixer

15g batch	20g batch	25g batch
2 min mix at 30 rpm	2 min mix at 30 rpm	2 min mix at 30 rpm
4 min mix at 30 rpm	4 min mix at 30 rpm	4 min mix at 30 rpm
8 min mix at 30 rpm	8 min mix at 30 rpm	8 min mix at 30 rpm
12 min mix at 30 rpm	12 min mix at 30 rpm	12 min mix at 30 rpm
		1 min mix at 35 rpm
		4 min mix at 35 rpm
		1 min mix at 40 rpm
		4 min mix at 40 rpm
		1 min mix at 45 rpm
		4 min mix at 45 rpm

4.3.2 Mixing with "Known Difficult to disperse" Additive

For this set of trials Americhem provided an additive which was an undisclosed mixture of Poly(p-phenylene oxide) (PPO) and Acrylic styrene acrylonitrile (ASA) with a brown pigment added. This masterbatch is typically used to create wood grain effects within polystyrene products and judged to mix poorly. It came in the form of small pellets only approximately three millimetres across and the aim of the trial was to see how well the mini mixer could mix this masterbatch into polyethylene. It was recommended to use polyethylene as the bulk medium to make it as difficult as possible for the masterbatch to mix into the polymer, with the hope of observing agglomerates of masterbatch held in the polyethylene and any changes to mixing quality.

The bulk material into which the masterbatch would be mixed was chosen as Stamylan LDPE (now Sabic LDPE 2602TX17). This material was in plentiful supply at the university and was typically used for foaming applications and therefore would provide a suitable contrasting bulk material.

4.3.2.1 Stamylan Polyethylene

Table 4.3 Stamylan Polyethylene properties [41]

Properties	Units	Values	Test methods
Melt flow rate (MFR) at 190 °C and 2.16 kg	g/10 min	1.5	ISO 1133
Density	kg/m^3	926	ISO 1183
Slip	mg/kg	800 O	SABIC method
Anti block	mg/kg	250	SABIC method
Modulus of elasticity	MPa	340	ISO 868
Hardness Shore D	-	48	ISO 306
Vicat softening temperature at 10 N (VST/A)	°C	99	DIN 53765
DSC test – Melting point	°C	113	DIN 53765
DSC test – Crystallization temperature	°C	103	DIN 53765
DSC test – avg. Heat of fusion	J/kg	123	DIN 53765

4.3.2.2 Experimental conditions

Each batch that was processed comprised of a 20g mix containing 98% polyethylene and 2% Americhem brown masterbatch with 0.3% moisture content. This concentration was recommended based upon the company's own usage and experience with the masterbatch.

The mixer was operated so that the set temperatures for the case (zone 1) and the die (zone 2) were 160°C respectively.

After each batch that was processed three 20g purge batches of virgin polyethylene were completed to flush out any remaining masterbatch left within the mixer.

Table 4.4 Mixing conditions for Americhem additive

	Mixing Speed			
Mixing Duration (minutes)	20rpm	30rpm	40rpm	50rpm
	4	0.5	4	4
	8	1	8	8
	12	4	12	12
		8		
		12		

4.3.3 Mixing with Carbon Black

For these trials a different property was investigated to determine the quality of mixing of materials produced by the mini mixer. This was the electrical conductivity induced into a polymer by the addition of carbon black. This property was chosen because it was a physical property of the polymer that could have a quantifiable analysis performed. Unlike the previous trials which were more qualitative. A full comparative study was performed in this trial, between the mini mixer and the standard mixers described in section 4.4.

The additive evaluated was that of Ketjenblack EC-200J carbon black. This additive is typically used to induce conductivity into polymers and was supplied via Whittakers Technical Plastics. The bulk polymer used for these trials was that of HG395 MO Borealis Polypropylene, as recommended by Whittakers Technical Plastics.

4.3.3.1 Ketjenblack EC-200J Carbon Black

The ketjenblack carbon black is used as an additive to induce electroconductivity, with the following specifications as found on the manufacturers product guide sheet. [42]

Appearance	Black free flowing pellets
Pore Volume (DBP)	310-345 ml/100g
Iodine adsorption	740/840 mg/g
Moisture	0.5% max
Volatiles	1.0% max
Ash	0.05% max
Fines <125 micron	7% max
Grit content	30 mg/kg max
pH	8-10
Apparent bulk density	125-145 kg/m^3
Approximate surface area	800 m^2/g (BET)

4.3.3.2 HG395 MO Borealis Polypropylene

As stated in the manufacturer's data sheets[43], HG385MO is a propylene homopolymer intended for use in injection moulding applications. With excellent flow properties and a narrow molecular weight distribution. The manufactures have combined it with an antistatic and slip formulation to allow short cycle times, good demoulding properties and low dust attraction.

Physical properties

Appearance: Solid granules, odourless.	Colour: Natural
Melting point: 130 - 170 ºC	Ignition temperature: > 300 ºC
Density: 0.9 – 1.0 g/cm3	Solubility: Insoluble in water.
Bulk Density: 0.5 – 0.6 g/cm3	

Table 4.5 Typical HG395 MO Borealis properties

		Typical value	Unit
Density		910	kg/m3
Melt Flow Rate	(230 ºC/2.16kg)	25	g/10 min
Tensile Stress at Yield	(50 mm/min)	36.5	MPa
Tensile Strain at Yield	(50 mm/min)	8	%
Tensile Modulus	(1 mm/min)	1750	MPa
Charpy Impact Strength, notched	(+23 ºC)	3.5	kJ/m2
Hardness, Rockwell		98	R-Scale
Heat Deflection Temperature	(0.45 N/mm2)	115	ºC

4.3.3.3 Conditions within Mini Mixer

Batch size: 25 grams

Temperature: 170 ºC for barrel (zones 1) and die (zone 2).

Table 4.6 Mixing conditions for 4 minute residence time

		Carbon Black Concentration wt%						
		2.5%	4%	5%	5.75%	6%	6.75%	7.5%
Speed	20 rpm	*	*	*	*	*	*	*
	30 rpm	*	*	*	*	*	*	*
	40 rpm	*	*	*	*	*	*	*
	50 rpm	*	*	*	*	*	*	*
	60 rpm	*	*	*	*	*	*	*

N.B. Speed of the mixing elements is 3.45 times that of the speeds shown above due to gearing.

Table 4.7 Mixing conditions for 1 minute residence time

		Carbon Black Concentration wt%							
		2.5%	4%	5%	5.5%	6%	6.5%	7%	7.5%
Speed	20 rpm	*	*	*	*	*	*	*	*
	60 rpm	*	*	*	*	*	*	*	*

The discharge speed for the mixer was fixed at 20 rpm for each batch. The mixer was purged between each new set of mixing concentrations.

A small amount of polymer was charged into the mixer before any carbon black could be charged. A portion of the carbon black was charged, followed by a quantity polymer pellets so that the material could then be pushed down the feed port into the mixer cavity. This method of feeding materials would continue until it was all charged. This was because it was impossible to add the two materials together without finding it difficult to push the material down the feed port. The polymer charge would clear the feed port of the carbon black charged so that the next portion could be fed. This process could take up to 2 minutes to perform.

Comparative Measurement with other Mixers

The purpose here was to compare the performance of the mini-mixer with that of a laboratory device widely used for research and formulation, the Haake and two larger scales co-rotating twin screw extruders, a 19mm APV MP19TC (L/D=25) and a 40 mm Betol BTS40

(L/D=29). The design details of these 3 machines can be found in section 4.4. We used carbon black Ketjenblack EC-300J as the pigment to be distributed and dispersed in the polymers and we measured the extent of its mixing into the polymer by measuring the change in electrical resistance as we increased the concentration of carbon black. We used this method of assessing and comparing performance because of its extreme sensitivity to dispersive mixing. The change in electrical resistance of semi-conducting and antistatic compounds is very sensitive to changes in the degree of dispersion and unless the same degree of dispersion that can be achieved in the larger machines at a given concentration is achieved in the laboratory scale devices at the same concentration, the formulation exercise in the laboratory will be off- specifications.

4.4 The Comparative Mixers

The mini mixer had its performance compared with three other machines.

- The HAAKE mini lab
- A 19 mm APV co-rotating twin screw
- A 40 mm BETOL co-rotating twin screw

These machines cover a range of scales from 0-5g with the HAAKE, to 0-5 kg/hr for the APV and 0-10 kg/hr with the BETOL. The comparison of equipment was primarily done using carbon black as the additive. It was also necessary to develop a system to feed the fine carbon black into the APV and BETOL twin screw extruders. The development of these two devices will also be described here.

4.4.1 The Haake

The Haake mini lab is a machine that has been developed by Thermo Scientific and has been marketed as a machine ideal for compounding expensive materials on a small scale for laboratory studies, such as nano-composites, bio polymers, pharmaceutical additives, etc.

The system comes with the following basic features: -

- Co and Counter rotating conical screws
- Pneumatic feeding system
- LCD screen for display
- A bypass for circulation of material
- Some basic automatic control
- Air and water cooling capability

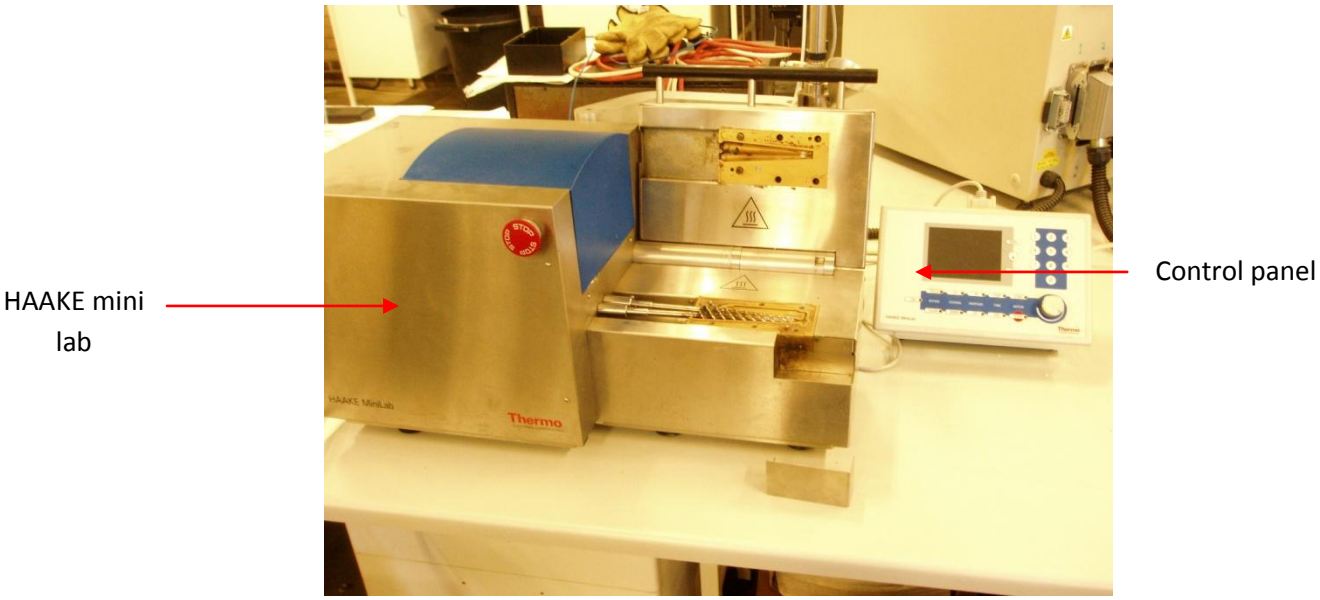


Figure 4.3 Overall view of HAAKE Minilab

It is possible to have the minilab integrated with a computer for better control and install an injection moulding system as well as a continuous feed system.

The system available within the Polymer IRC at the University of Bradford was that of the basic system without any additional options. Table 4.7 lists the manufacturer's specifications for the mini lab. The screws are intermeshing and conical in design and attach to the drive shafts via key ways and loose sleeves. The geometry of the screw channels making sure that the shafts do not slip out of position. The bypass valve enables the user to specify whether recirculate material or discharge through the die. These details can be seen in Figure 4.4.

Table 4.8 Haake Technical Specifications[5]

Motor power	kW	0.4
Speed range	min-1	10 – 360
Torque range	Nm	0 – 5
Overload protection		Motor control
Screw diameter	Mm	5/14 conical
Screw length	Mm	109.5
Integrated heating zones		1
Heating capacity	W	800
Max. temperature	ºC	350
Mains supply	V	115/230 switchable
Dimensions (W/D/H)	Mm	655 x 470 x 590
Weight	Kg	70

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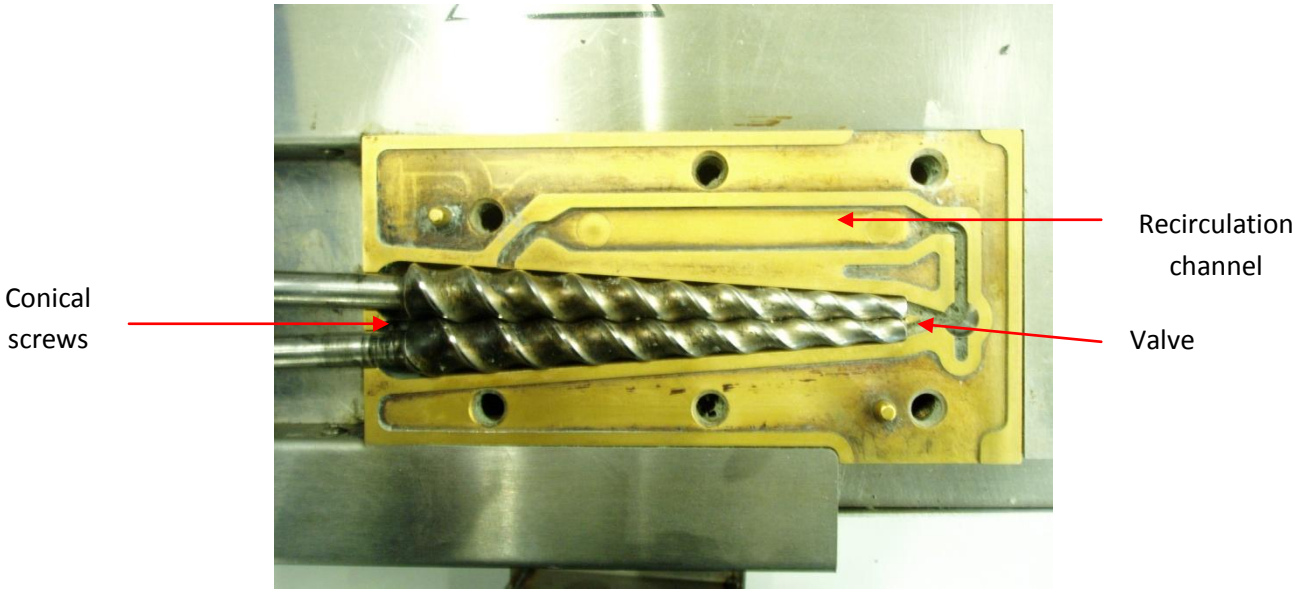

Figure 4.4 Details of HAAKE Minilab screw arrangement.

The pneumatic feeder was found to jam repeatedly when fine powders, such as carbon black, were introduced. A manual plunger was fashioned to enable manual feeding of the polymer and carbon black powder could be achieved.

The recirculation channel was also found to retain a significant portion of the charged material after discharge. From a 3g charge, approximately 2g of material would be discharged with the remainder held in the recirculation channel.

Experimental conditions

The experimental conditions used in the Haake for comparison. N.B. The mixing speeds stated are based on the geared mixing speed of the mini mixer cams.

- Operating temperature: 180 degree C
- Mixing Speeds: 70rpm, 105rpm, 140rpm, 175rpm & 210rpm.
- Carbon black concentrations considered (wt%): 2.5%, 5%, 6% & 7%.
- Residence times considered: 1 minute & 4 minutes.

Method of operation

1. Switched on the machine; ensuring casing was fully bolted down.
2. Set the desired temperature, which was in this case 180 deg C.
3. Allowed the machine to warm up to set temperature, before pressing the Calibrate button.
4. Set mixing speed to 20 rpm and pressed start to engage the motor.
5. Manually charged the polymer and carbon black via the charge cute using a manual plunger. Charged a little polymer first, following by carbon black. Repeated until all material was charged.
6. Once all material was fully charged, manually increased speed to the desired value for mixing and allowed to recirculate for the desired residence time.
7. Switched to flush to discharge the material. This rotated the valve by 90 degrees to block the entrance to the recirculation channel and divert the flow through the 2 mm die.

8. The first batch was scrapped and another prepared. Steps 4 to 7 are repeated to ensure that any material left in the recirculation channel is of the same concentration as the subsequent batches to be tested.

4.4.2 The APV 19mm

This table mounted twin screw has been typically used for small scale compounding of two materials, when low quantities of material have been required or provided. The specifications of the extruder can be found in Table 4.8.

Table 4.9 Technical specifications of APV MP19TC 19mm twin screw extruder

L:D ratio		25:1
Temperature range	ºC	0 - 300
Speed range	rpm	0 – 500
Feed system		Two Spiroflux feeders

The spiroflux feeders are both located above the feed port to the twin screw and can be calibrated to charge material at the desired rate to achieve the desired mixture composition to be compounded. The machine is equipped with a standard screw arrangement as provided by the manufacturer which can be seen in Figures 4.5 and 4.6.

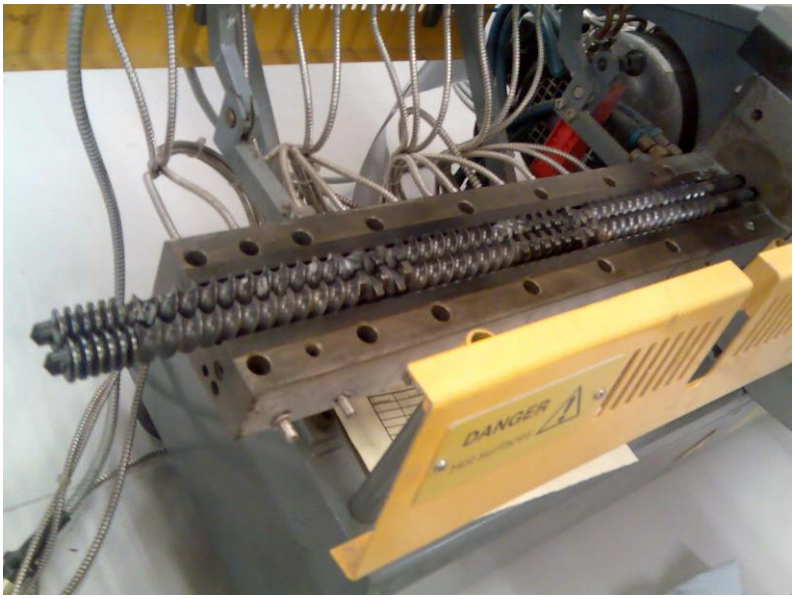

Figure 4.5 APV Screw arrangement

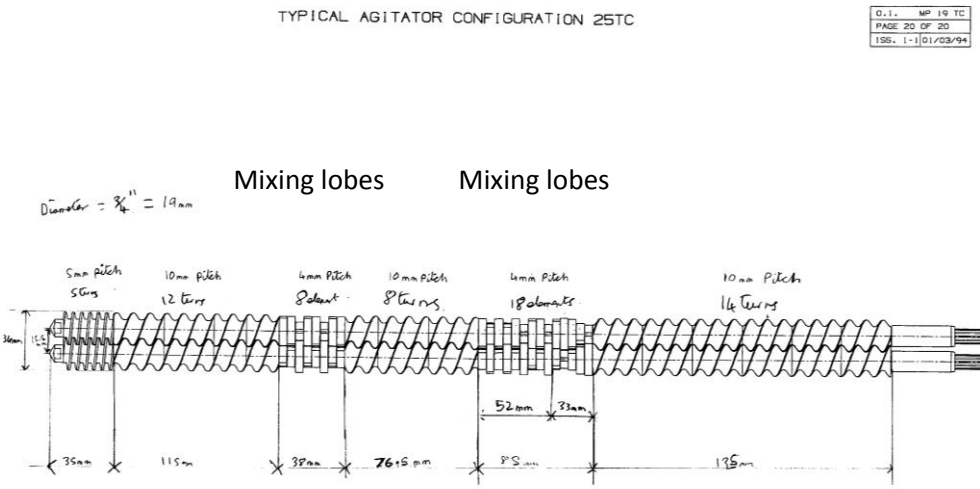

Figure 4.6 Dimensions of APV screw arrangement[44]

The arrangement comprises of a metering section of intermeshing screws, followed by the main section of mixing lobes. This is then followed by another metering section of intermeshing screws which transfer material into the next section of mixing lobes. From here material is then pumped towards the die by another section of intermeshing screws. Figures 4.7 and 4.8 provide the details of the individual elements that make up the screw arrangement showing in Figure 4.6.

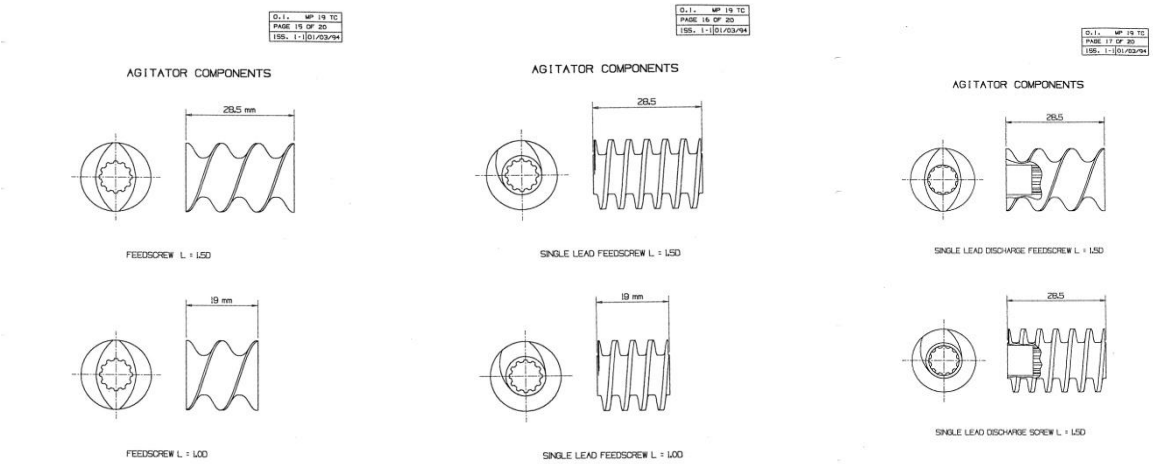

Figure 4.7 Details of APV screw sections[44]

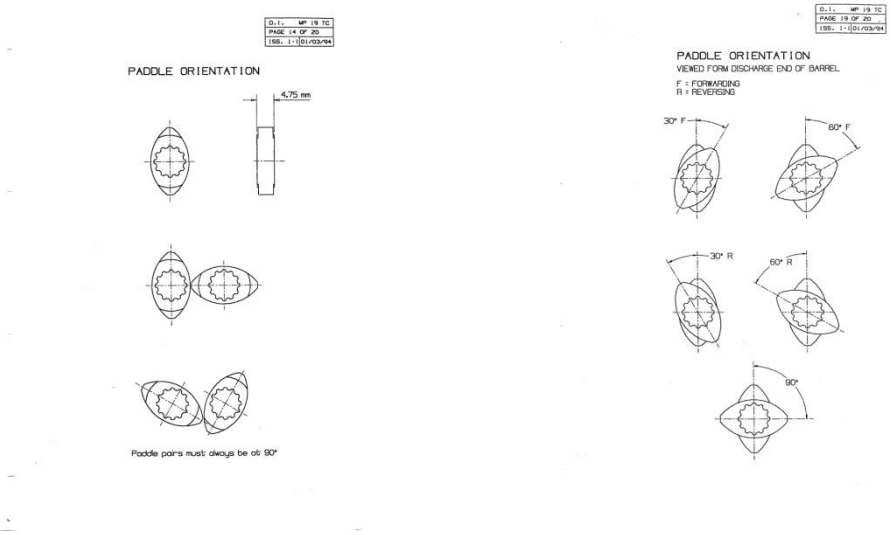

Figure 4.8 Details of APV Mixing Paddle Orientation[44]

Experimental conditions

Temperatures: 170 º C at the feed zone and then 180 º C down the rest of the extruder.

Table 4.10 Carbon black concentrations and screw speeds use in APV 19mm twin-screw.

		Carbon Black Concentration wt%						
		4%	5%	5.5%	6%	6.5%	7%	7.5%
Speed	80 rpm	*	*	*	*	*	*	*
	120 rpm	*	*	*	*	*	*	*
	160 rpm	*	*	*	*	*	*	*
	200 rpm	*	*	*	*	*	*	*
	240 rpm	*	*	*	*	*	*	*
	280 rpm	*	*	*	*	*	*	*
	320 rpm	*	*	*	*	*	*	*
	360 rpm	*	*	*	*	*	*	*
	400 rpm	*	*	*	*	*	*	*

Method of operation

The twin screw was operated under starved conditions. A custom made system to feed the carbon black into the twin screw was required as none of the feed hoppers available could regulate a constant flow of carbon black into the machine on the scale of quantities needed.

Once a suitable feed system was devised for the carbon black, see section 4.4.4, it was determined that due to scale of operation the speed of the carbon black feeder would remain constant and that flow of polymer would be changed to provide the concentration changes required for the experiment.

Due to the eventual scale of the carbon black feeder the small auger for feeding polymer pellets was used during the experiments. Because the carbon black was such a fine powder

it was decided that the carbon black feeder would operate fixed at its maximum discharge rate and the amount of polymer fed into the twin screw would be varied to provide the concentration changes.

Calibration and residence time data

This section deals with the calibration data for the APV 19mm Twin screw.

The twin screw extruder has two feed hoppers for polymer pellets. One makes use of a large auger, another uses a smaller auger. Each one using a controller that presented the speed that the motor was running at as a percentage.

The two feed hoppers were available and calibrated using HG395MO Borealis Polypropylene pellets, to determine which would be used for the experiments. The hoppers had a facility where the feed chute to the twin screw could be blocked off and the pellets redirected to a bag for weighing.

Since the APV twin screw machine operates in a starved feed condition, it was necessary to find the mass flow rate of pellets that would subject the twin screws motor to high levels of torque and trip the machines automatic motor cut out. This cut out value would be different for each screw speed and would determine the lowest speed the twin screw would be operated at for the experiments. The feeder using the largest auger was used to conduct these tests.

A tracer of carbon black was added and the time taken for tracer to become evident at the die of the extruder was recorded. This was done for each screw speed and polymer feed rate tested in the extruder and the results can be seen in table 4.14.

Table 4.11: Large Auger Calibration Data.

% speed	Time s	Mass g	Mass Flow rate g/min	Average g/min
20	120	61.8	30.9	
20	120	62.4	31.2	31.1
20	120	62.1	31.1	
40	120	111.2	55.6	
40	120	110.5	55.3	55.5
40	120	111.0	55.5	
50	120	134.0	67.0	
50	120	133.6	66.8	67.0
50	120	134.3	67.2	
60	120	159.2	79.6	
60	120	159.3	79.7	79.5
60	120	158.7	79.4	
80	120	205.1	102.6	
80	120	206.8	103.4	103.0
80	120	205.8	102.9	
99	125	272	130.6	
99	125	257.6	123.6	126.3
99	125	259.9	124.8	

Table 4.12: Small Auger Calibration Data

% speed	Time s	Mass g	Mass rate g/min	Average g/min
20	120	22.3	11.2	
20	120	21.2	10.6	10.9
20	120	22.1	11.1	
40	120	41.6	20.8	
40	120	42.8	21.4	21.3
40	120	43.5	21.8	
50	121	53.7	26.6	
50	120	55.5	27.8	27.2
50	120	54.7	27.4	
60	120	67.2	33.6	
60	120	67.8	33.9	33.6
60	120	66.5	33.3	
80	120	88.7	44.4	
80	120	90.2	45.1	44.9
80	120	90.2	45.1	
99	125	114.4	54.9	
99	125	116.7	56.0	55
99	125	115.6	55.5	

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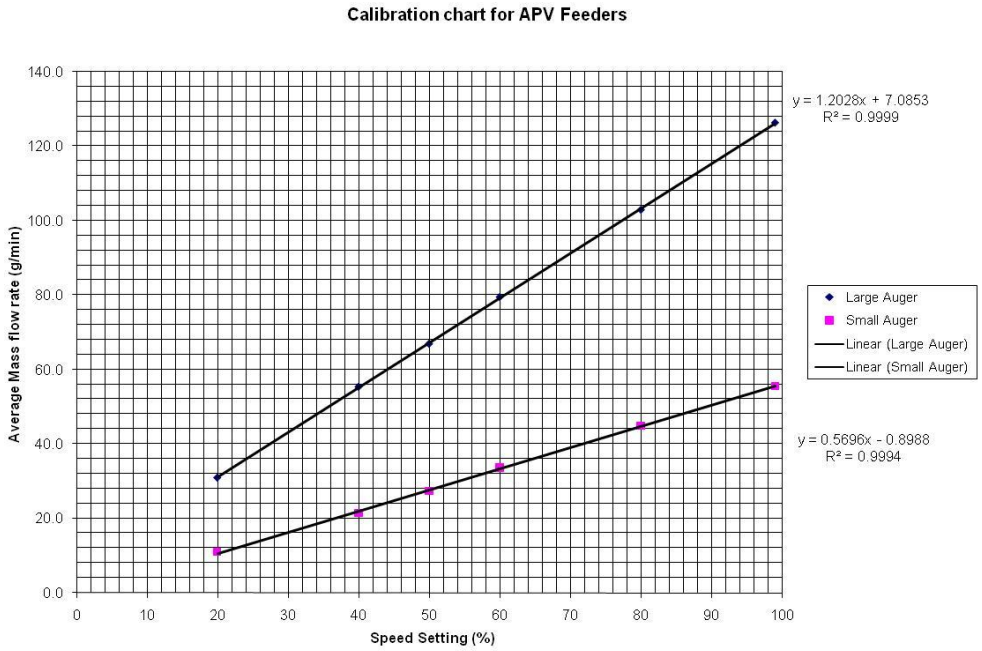


Chart 4.1: Calibration chart for APV feeders.

Table 4.13: Twin screw motor trip data.

Twinscrew speed (rpm)	Auger Speed (%)
20	32
40	40
60	48
80	57
100	65
200	82

Table 4.14 Residence time data for APV 19mm twin screw

Twin screw speed (rpm)	Time (seconds)
40	90
80	66
120	59
160	55
200	50
240	47
280	46
320	45
360	42
400	43

4.4.3 The Betol 40mm

The Betol BTS40 is an intermeshing co-rotating twin screw extruder used within the Polymer IRC at the University of Bradford for the majority of their needs that require the compounding of a large quantity of material. The machine has three K-tron feeders mounted on load cells, enabling the simultaneous feeding of three materials into the main feed port. Further down the extruder barrel if an additions port which allows direct feeding of powdered material onto the flights of the screw.

The key details of the twin screw can be found in Table 4.13.

The design of the screws is that of trapezoidal flights that intermesh closely. At points down the barrel the flights are replaced with either two or four barrier or trilobal mixing elements, which are detailed in Figures 4.7 and 4.8.

Table 4.15 Technical specifications of the Betol BTS40 Co-rotating twin screw extruder

L:D ratio		29:1
Temperature range	ºC	0 - 300
Speed range	rpm	10 – 200
Screws		Closely intermeshing trapezoidal flight design.

Additional details

- Addition feed port
- 3 K-tron loss-in-weight feeders mounted on load cells

Additive feed port

| |

Pitch	24	16	12	B4	16	16	T2	16	16	B4	16	16	B2	T4	12	12
Length (mm)	120	80	80	50	120	120	10	120	80	50	80	80	25	20	80	80

< Throat----------Die >

Figure 4.7 Element arrangement throughout the twin screw

N.B. B2, B4, T2 & T4 represent 2 or 4 barrel or trilobal elements

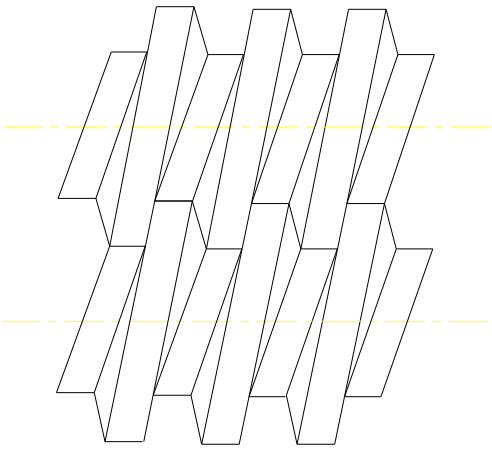


Figure 4.8 Details of the screw flights and mixing elements

Experimental conditions

Eleven temperature sensors were installed along the length of the twin-screw extruders barrel, starting at the feed port and ending at the die. For the polymer feed rate of 3 kg/hr the temperature was set to 180 ºC down the entire length. For the polymer feed rates of 5 kg/hr and then the higher rates of 7 kg/hr and 9 kg/hr the temperature from the 4th sensor onwards had to be increased to 190 ºC and then 195 ºC to prevent polymer backing up and flowing out of the carbon black additions port.

Table 4.14 indicates the conditions that were performed in the BETOL twin-screw, although it was found that feed rates of 7kg/hr and 9 kg/hr the screw speed of 50 rpm was too slow to prevent polymer melt building up and exiting the additions port of the twin-screw extruder as the carbon black was added. It was also found that the carbon black feeder couldn't consistently feed necessary quantity of carbon black to provide the 2.5% concentration necessary for the 3 kg/hr polymer feed rate.

Table 4.16 BETOL screw speeds and Carbon black concentrations

		Carbon Black Concentration wt%				
Polymer feed rate: 3kg/hr		2.5%	4%	5%	6%	7%
speed	50 rpm	n/a	*	*	*	*
	80 rpm	n/a	*	*	*	*
	110 rpm	n/a	*	*	*	*
	140 rpm	n/a	*	*	*	*
Polymer feed rate: 5kg/hr		2.5%	4%	5%	6%	7%
Speed	50 rpm	*	*	*	*	*
	80 rpm	*	*	*	*	*
	110 rpm	*	*	*	*	*
	140 rpm	*	*	*	*	*
Polymer feed rate: 7kg/hr		2.5%	4%	5%	6%	7%
Speed	50 rpm	n/a	n/a	n/a	n/a	n/a
	80 rpm	*	*	*	*	*
	110 rpm	*	*	*	*	*
	140 rpm	*	*	*	*	*
Polymer feed rate: 9kg/hr		2.5%	4%	5%	6%	7%
Speed	50 rpm	n/a	n/a	n/a	n/a	n/a
	80 rpm	*	*	*	*	n/a
	110 rpm	*	*	*	*	*
	140 rpm	*	*	*	*	*

Method of operation

The twin-screw was operated in starved feed conditions, with the carbon black fed at the additions port using the feeder custom made for this purpose, see section 4.4.4. The polymer was loaded into one of the K-tron feeders that are mounted above on load cells, from which its flow rate into the twin screw could be controlled to the desired values.

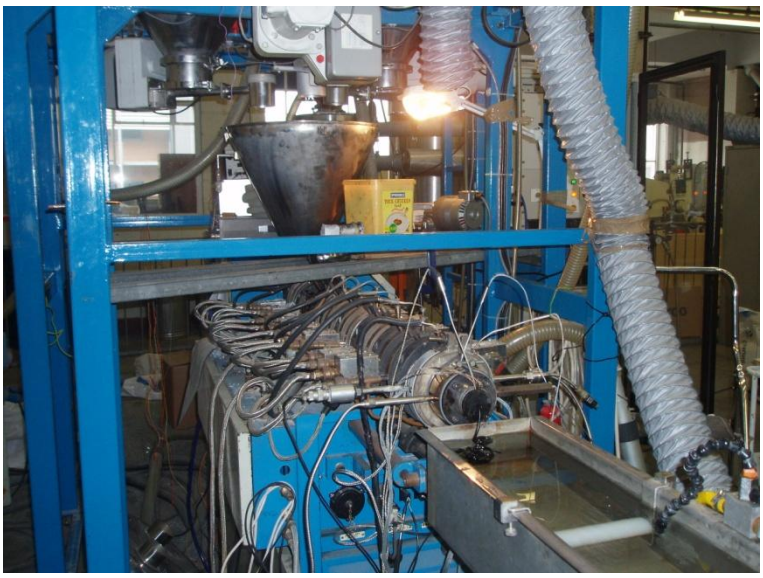


Figure 4.9 BETOL 40mm Twin Screw Extruder

Residence Time Data

The residence time of the carbon black additive was checked for the extruder. This was achieved by feeding virgin polymer into the extruder at a specified feed rate, while running the extruder at a specified mixing speed. A tracer of carbon black was added and the time taken for tracer to become evident at the die of the extruder was recorded. This was done for each screw speed and polymer feed rate tested in the extruder and the results can be seen in table 4.18.

Table 4.17 Residence time data

		Polymer feed rate			
		3 kg/hr	5 kg/hr	7 kg/hr	9 kg/hr
Screw speed	50 rpm	3 min 25 sec	2 min 40 sec	n/a	n/a
	80 rpm	2min 40 sec	2 min 4 sec	1 min 46 sec	1 min 32 sec
	110 rpm	2 min 18 sec	1 min 42 sec	1 min 29 sec	1 min 17 sec
	140 rpm	2 min 2 sec	1 min 29 sec	1 min 18 sec	1 min 17 sec

4.4.4 The Custom Designed Carbon Black Feeders

Two systems were designed to feed the fine carbon black powder, one each for the 19mm APV twin screw and the 40mm BETOL twin screw extruders.

Feed system for APV twin screw

A carbon black feeder had to be custom made as the quantities of carbon black required were so small that the smaller of the two auger systems was too large to use.

The feeder developed consisted of a metal spring, driven by a motor, being used as a screw conveyor to push the carbon black along a copper pipe so that it discharges from the end. For the purposes of calibrating the machine the carbon black was discharged into a cup for collection and weighing.

In this test a spatula was used to continually disturb the carbon black to stop the material bridging above the feed port of the screw conveyor. The pitch of the spring was about 5 mm with a wide angled feed hopper fashioned from cardboard and taped in place around an aperture cut into the copper pipe.

Figure 4.10: Carbon black feeder installed on APV twin screw.

Table 4.18: Carbon black feeder calibration data

Speed setting	Time (s)	Mass (g)	Mass rate (g/min)	Average (g/min)
15	120	3.0906	1.5453	
15	120	3.3432	1.6716	1.6274
15	120	3.3302	1.6651	
20	120	4.5614	2.2807	
20	120	4.5178	2.2589	2.2544
20	120	4.4468	2.2234	
25	121	5.4852	2.7426	
25	120	5.4987	2.7494	2.7310
25	120	5.4019	2.7010	
30	60	3.2254	3.2254	
30	60	3.2896	3.2896	3.2474
30	60	3.2273	3.2273	
35	60	3.2521	3.2521	
35	60	3.8294	3.8294	3.6219
35	60	3.7841	3.7841	

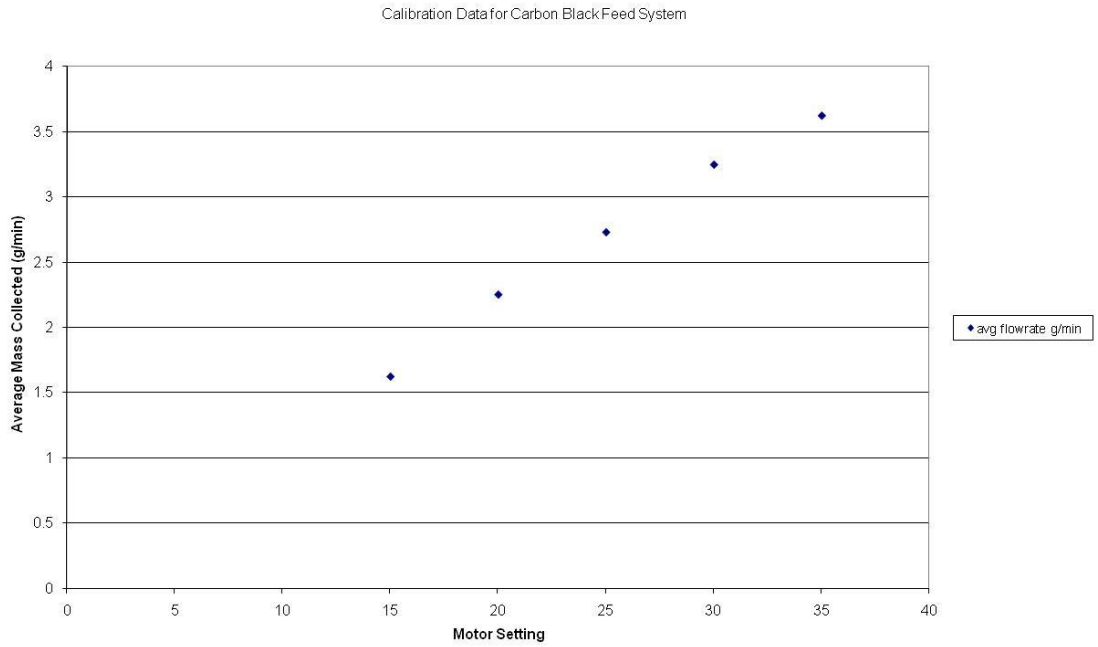


Chart 4.2: Calibration Chart for Carbon Black Feed System

Feed system developed for the BETOL twin screw

Figure 4.11 Carbon Black feeder for BETOL Twin screw

A carbon black feeder had to be custom made as there was no existing system to feed the powder into the additions port of the BETOL twin-screw. This design was a larger version of the one built for the APV twin screw.

Table 4.19 Calibration data for BETOL carbon black feeder

% Setting	Time (s)	Mass (gm)	Mass Flow (g/hr)	Mass Flow (kg/hr)
10	300	10	120	0.12
15	330	20	218	0.22
20	271	23	306	0.31
25	240	27	405	0.41
30	270	36	480	0.48
35	240	36	540	0.54
40	240	41	615	0.62
45	240	47	705	0.71
50	240	52	780	0.78
60	255	67	946	0.95
70	240	69	1035	1.04

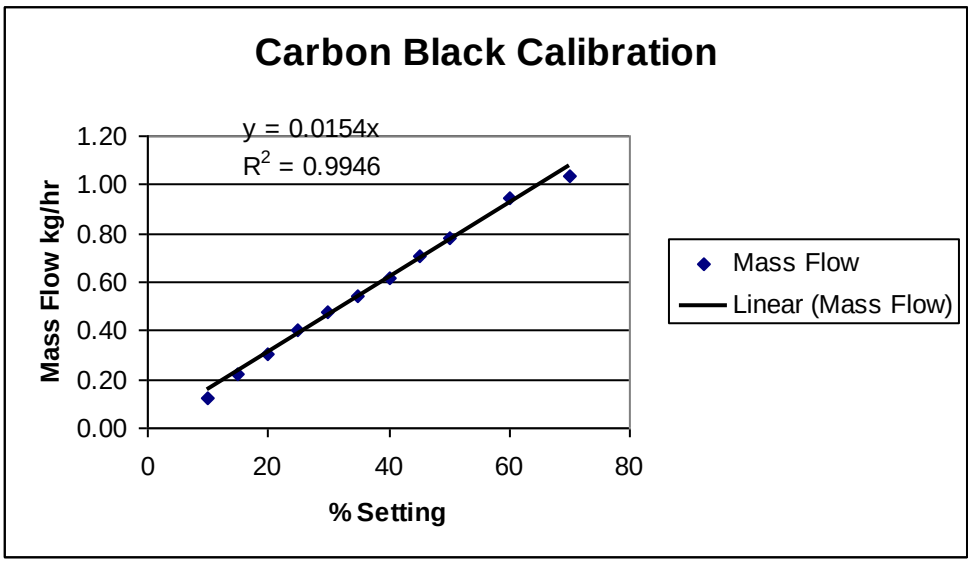


Chart 4.3 Calibration chart for BETOL carbon black feeder

4.5 Measurement of Mixing

In this section I will explain the measurement methods used to analyse the performance of the mixer.

The first method used to analyse the samples produced was through inspection using a microscope, BS ISO 18553:2002 as a guide[45], and making use of the OPTIMAS image analysis package.

For this there are a number of techniques that were used for preparing the samples for inspection, these are summarised as follows:-

- Preparation by Blown Film
- Preparation by Microtoming
- Preparation by use of a Thin Film Maker
- Preparation by forming a pressed Plaque

In this section I will discuss these techniques and the use of the OPTIMAS imaging software.

The second method used to measure the quality of mixing was through observing the change in a property of interest within the polymer; in this case the conductivity of the resultant extrudate was measured.

4.5.1 Microscopy

The technique typically used from an industry perspective is comparing the colour of the product against the standard with the naked eye. This involves taking a pressed plaque of the product and holding it against the standard under the same lighting conditions. Through the use of a microscope a more detailed visual comparison can be done, as agglomerates and striations typically become more apparent. The following techniques described are some of the methods used to prepare samples for microscopic analysis.

4.5.1.1 Preparation of Sample by Blown Film

The method involved creating a blown film of the sample. This is done by taking the extrudate and "letting it down" to 1% in virgin polymer and running it through a blown film extruder. The resultant film is then collected. A section is cut and affixed to a microscope slide with Canada balsam so that it can be inspected under the microscope for agglomerates and striations.

4.5.1.2 Preparation of Sample by Microtoming

The method involves taking a random section of the sample and using a microtome to slice thin slivers of material which can then affixed to a slide with Canada balsam and inspected under a microscope.

4.5.1.3 Preparation of Sample by Thin Film Maker

The method involves taking small pieces of the extrudate from the mixer and using a thin film maker and a press to create discs ranging in thickness from 25 microns to 250 microns. These discs can then be inspected under the microscope.

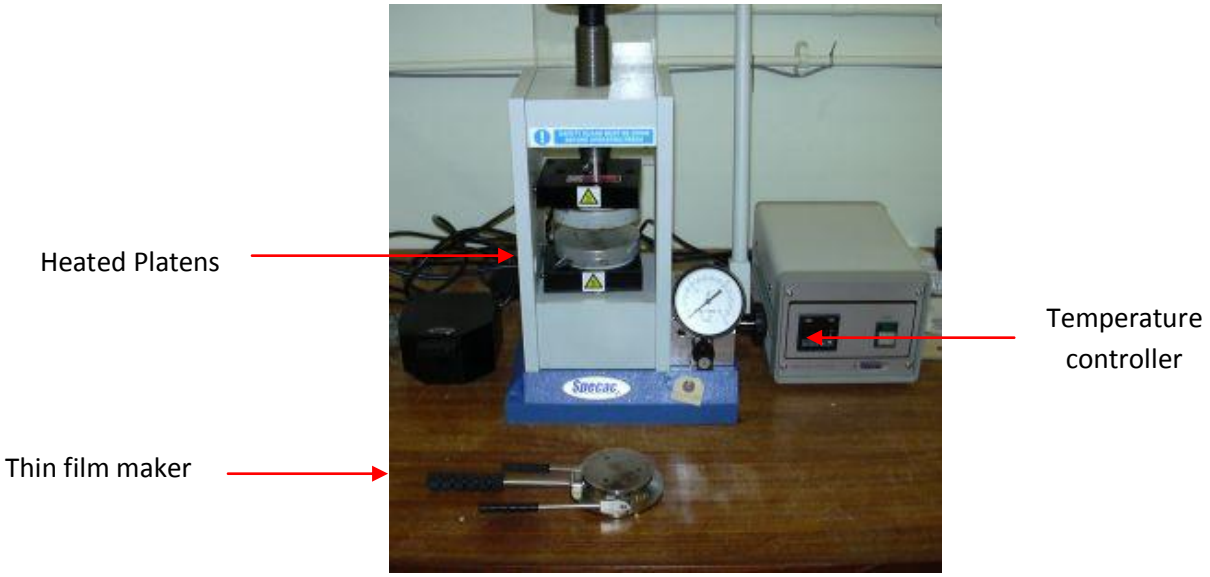


Figure 4.12 Specac Thin Film Maker and Heated Press

4.5.1.4 Preparation of Sample by Pressed Plaque

For the analysis of the samples containing americhem a slightly different technique to that used for the creation of thin films. A 2.5 cm section of extrudate would be taken randomly and using a custom made mould, pressed into a 1 mm thick plaque. This plaque could then be viewed under a microscope and images taken for analysis. For each batch three samples would be randomly generated and from each sample three random images would be generated.

Figure 4.13 A 10 ton press and samples.

4.5.1.5 OPTIMAS Software

Images of the samples viewed under the microscope were taken using a camera attachment. These images were then analysed using the OPTIMAS software to determine the size distribution of any agglomerates found and their locations relative to one another. The software is capable of calculating the area of irregular shapes and returning a diameter of a sphere with the equivalent surface area, which makes comparisons of particular size much easier.

Calibration was carried out using an image of a 1mm graticule taken at 2.5x magnification under the microscope. This enables accurate measurement of particle size and location. The OPTIMAS software was configured so that the region of interest is the entire image (except for a black border that the image capture software adds), from which it extracts the particle area, the coordinates of each particle centroid and calculates the diameter of an equivalent spherical particle. All images were taken at 2.5x magnification and each image was 3 mm x 4 mm in size.

Within the software an image threshold is set, which enables the software to focus on the particles present in the foreground of the image and exclude fainter background particles. This threshold is very much dependant on the lighting conditions used when the image is taken; therefore the lighting conditions were kept constant as possible when images were taken under the microscope for analysis by the software. This proved to be difficult as we are taking a two dimensional image of a three dimensional object, so that as smaller particles are dispersed throughout the sample, they block more of the light passing through the sample.

From this data a size distribution based on the equivalent sphere diameter can be generated to analyse the dispersion within the image sample. An overall particle size distribution was then generated for the batch by averaging all the frequency values for each particle size across all nine images. This method smoothes out large variations between the size distributions for the individual images to give a general size distribution curve for the batch.

This is because you will see some variation between the images depending on where they are taken from the strand as you may find one of the image samples is dominated by a single large particle while the other image samples are not.

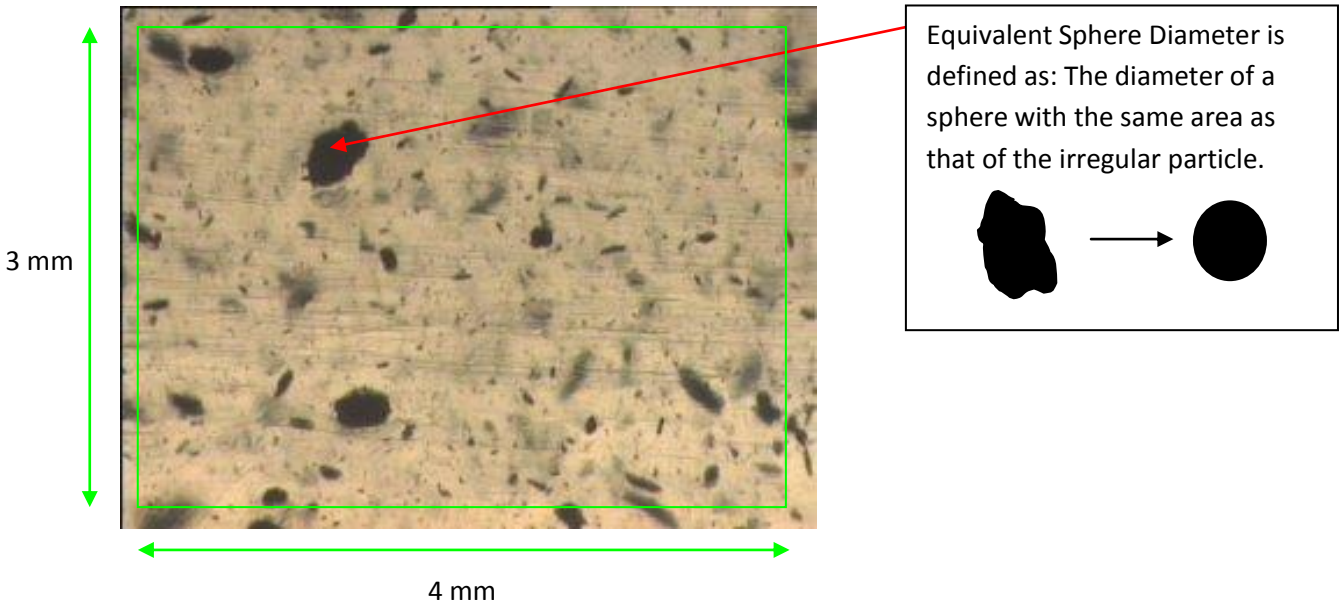


Figure 4.14 Example of OPTIMAS analysis

4.5.2 Conductivity measurements

The measurement of semi-conductivity[46-50] was performed by taking a strand of extrudate with a fixed and known length. The sample is then prepared by being cleaned with acetone before the ends are coated with silver paint to ensure a good electrical contact. The sample is then connected to a Keithly Instruments Solid State Electrometer (610C) which passes 9 volts through the sample enabling the resistance to be viewed and recorded. This data can then be converted into resistivity values to allow ease of comparison.

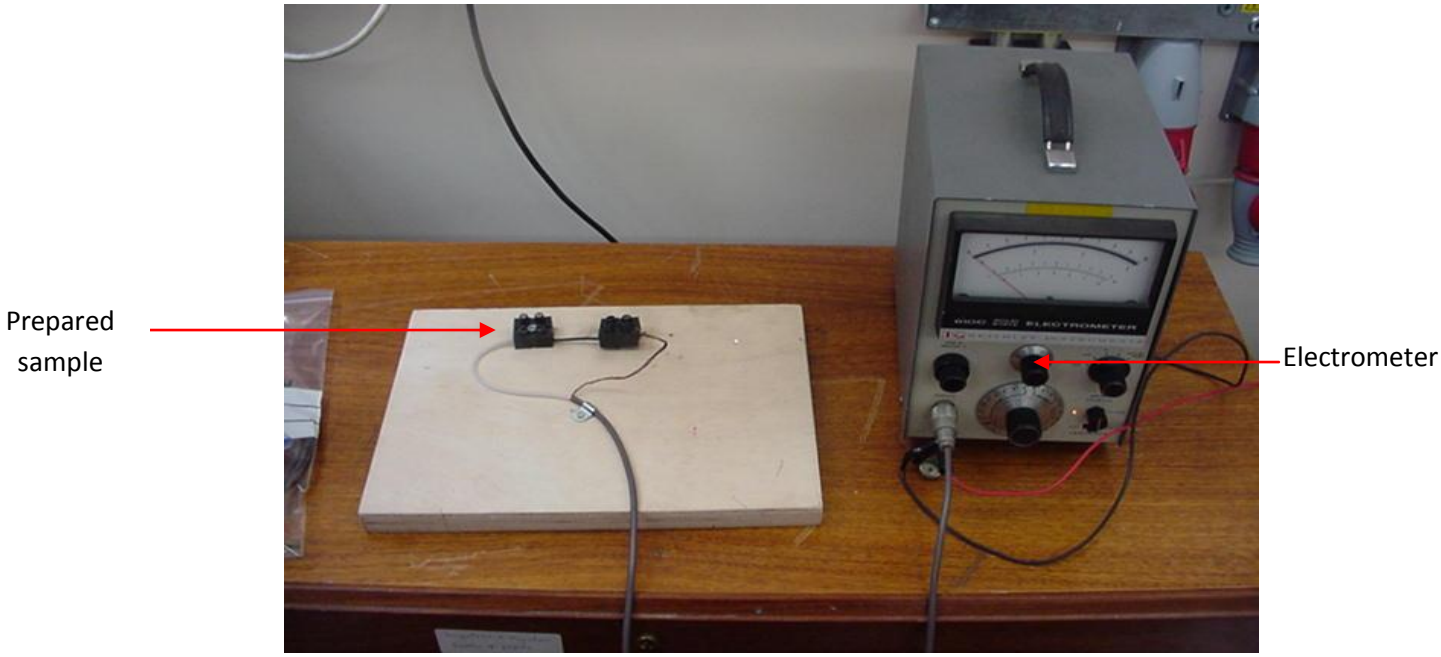
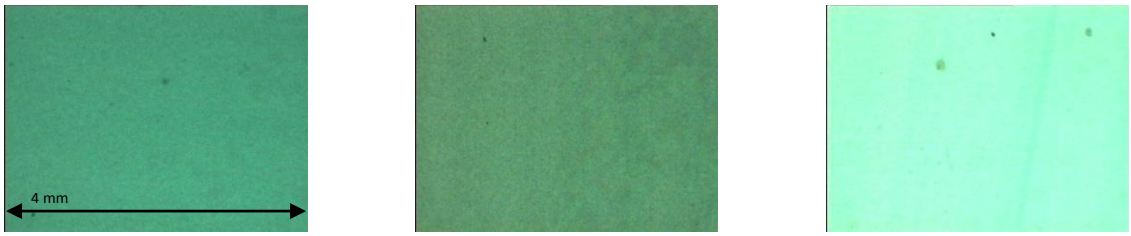


Figure 4.15 Keithly Instruments Electrometer (610C)

4.6 Experimental Results

4.6.1 Colour masterbatch

In section 4.5, the various methods of analysing these initial experiments were outlined. When it came to looking at the samples under the microscope at x10 magnification what stood out straight away was that it was hard to distinguish any, if at all, changes in mixing quality. Examples of these can be seen in Figure 4.16.



30 rpm 45 rpm Colloids Standard

Figure 4.16 10x Magnification Microscopic Image (4mm x3mm) of blown film sample produced in mixer and Colloids Standard

The colour of the samples are darker compared to the standard provided, but this could be down to different thicknesses of film and lighting problems. The important consideration in Figure 4.16 is not colour but the presence of "pigment blobs" if any which are indicative of poor mixing. The occasional blobs that were present in the blown film samples produced at Colloids Ltd, were suspected as specks of degraded polymer from the machine. When a film of pure polyethylene was produced using the same machine, to check if this was the case, it was found to be filled with burnt specks of polymer, as can be seen in Fig 4.17. This made it difficult to distinguish which specks were unmixed masterbatch and which were degraded material from the screw of the blown film machine.

Figure 4.17 Polyethylene Colloids Sample

Clearly, this method is not satisfactory to assess mixing and the method of creating pressed films was tried, see Figure 4.18. This showed that there was some unmixed material present but again very little if no changes could be found between samples.

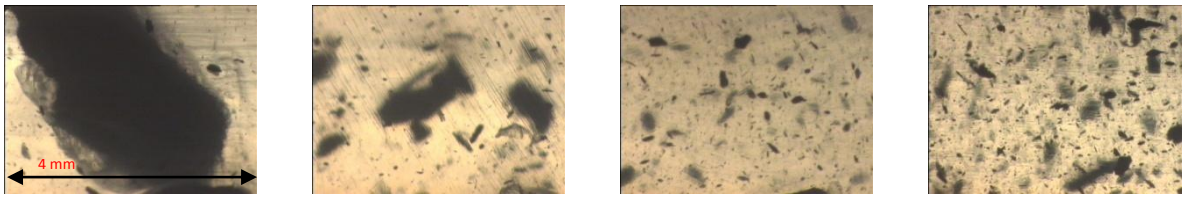
30 rpm 45 rpm

Figure 4.18 Pressed film samples at 10x magnification

In some ways this is not surprising as the act of melting and pressing a thin film would cause reorientation of the material. With these samples looking so similar regardless of the conditions they were subjected to, a new additive was sought to allow a more quantifiable analysis to be performed. This is when the tests using the Americhem masterbatch were conducted.

4.6.2 Americhem

These experiments proved to be more successful at demonstrating changes in mixing quality within the mini mixer. From the start noticeable changes in mixing quality could be seen with the naked eye as processing conditions were changed. Figure 4.19 shows sample images of the changes in mixing quality for batches mixed for 4 minutes at various mixing speeds. Clearly, as speed is increased, we observe the dispersion of agglomerate into a larger number of finer particles. This is evidence that mixing was occurring and improving with mixing speed and time.



20 rpm 30 rpm 40 rpm 50 rpm

Figure 4.19 Americhem 4 minute mixing samples (4mm x 3mm image)

This enabled a quantifiable analysis to be performed on the samples created, by making use of the OPTIMAS software to perform number counts and particle size measurements on the samples so that particle size distributions can be generated. The images of the samples that were taken can be found in appendix A, tables A1 to A42.

These images clearly show that as the mixer is run faster, and as a result the shear rate is increased, the Americhem masterbatch in the mixture was broken down further into smaller particulates. As the mixer was left longer to mix, this also contributed to an increase in

smaller particles being present within the samples. This can be seen clearly in the three graphs of Chart 4.4 to 4.6.

The graphs clearly show this trend, which logically should be expected. The likely reason for the ability of the mixer to so thoroughly disperse the pellets of masterbatch and distribute them into the polymer comes from the small gap between the wall of the mixer and the mixing cams, a distance of 0.125 mm. This small gap between the wall and the mixing cams, allows material to be squashed by the shear rates generated as material is forced around the walls of the mixing cavity.

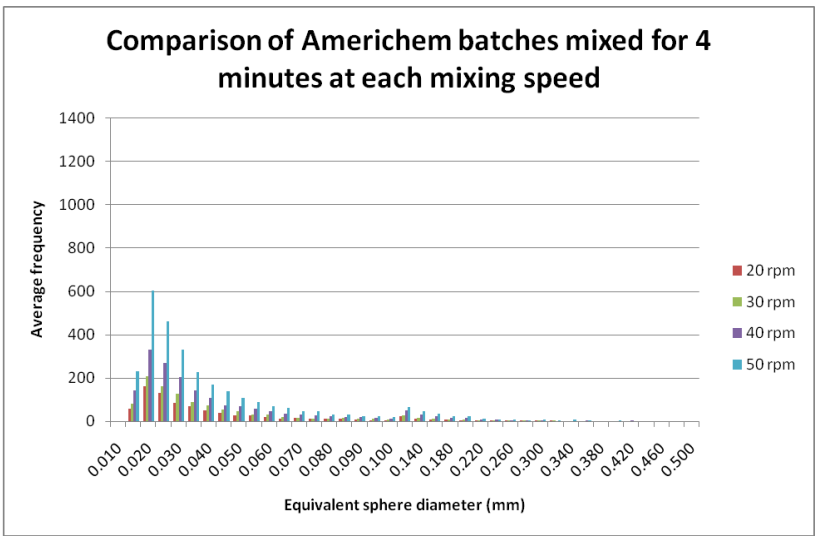


Chart 4.4 : Americhem Particle size distribution for 4 minutes mixing

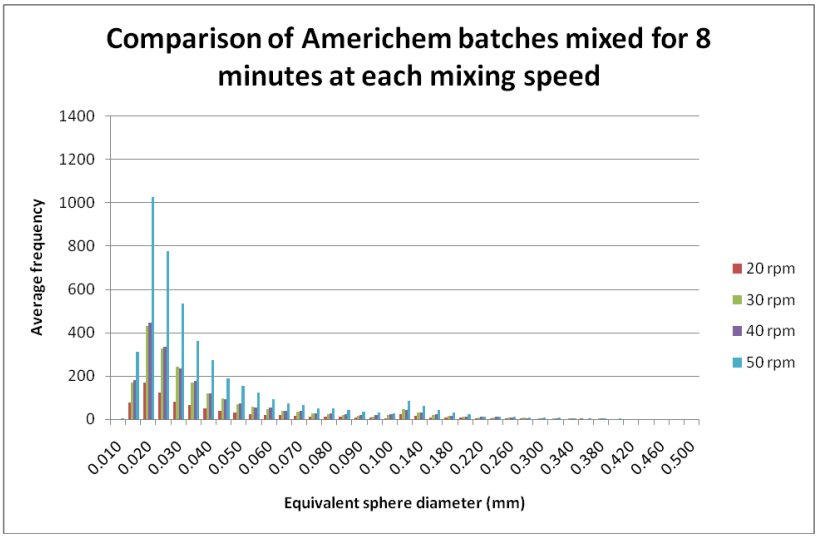


Chart 4.5 : Americhem Particle size distribution for 8 minutes mixing

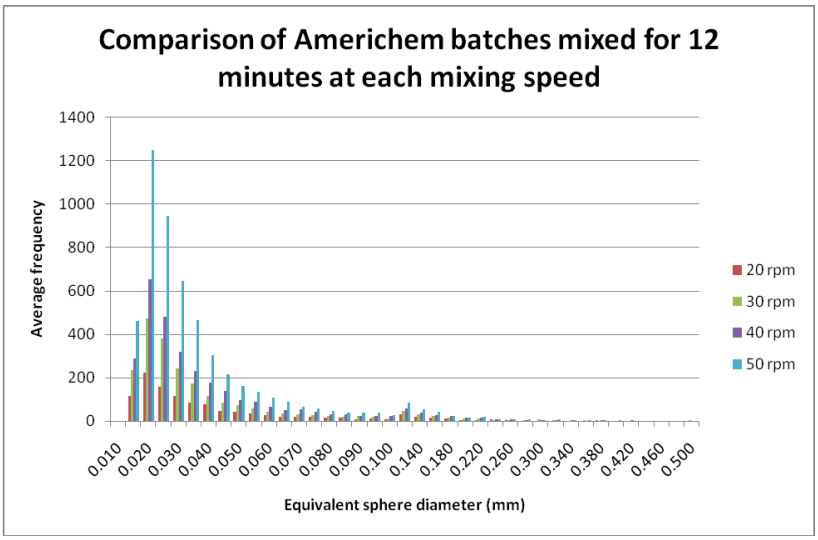


Chart 4.6 : Americhem Particle size distribution for 12 minutes mixing.

Charts 4.7 and 4.8 show how the nominal equivalent particle size of 0.02 mm varies with speed and time, showing an almost linear relationship in particle size reduction. In conclusion for this important part of the experiments, the minimixer was able to disperse efficiently an additive into a polymer melt, known to be difficult to achieve in industrial devices. Indeed Americhem additives are used to grain polymer to give the appearance of wood. In addition, this part of the research enabled to assess numerically the improvement

in mixing with speed and residence time, in other words underpin performance with data on size reduction of agglomerates.

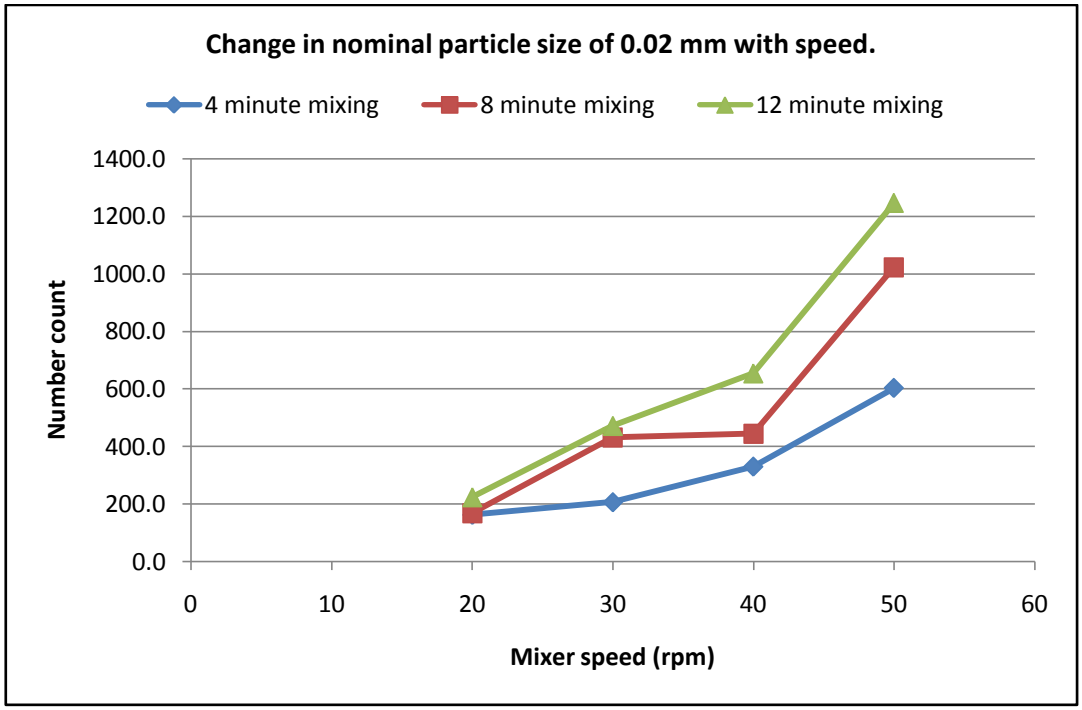


Chart 4.7 Change in Americhem nominal size with speed

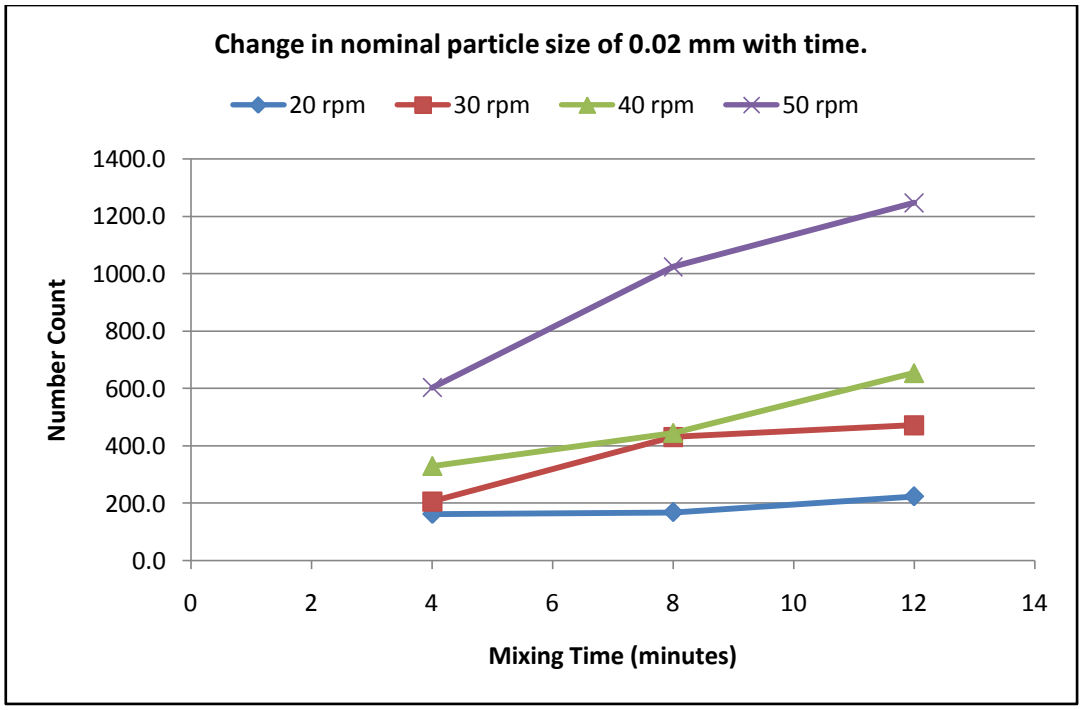


Chart 4.8 Change in Americhem nominal size with time

4.6.3 Carbon black

With the carbon black experiments the aim was to measure the electrical resistance of the samples produced, more precisely the minimum % loading necessary to create conductivity (percolation threshold). As conductivity is closely linked with electrical paths this is a very good indication of mixing uniformity. Would the minimixer induce percolation threshold at a % carbon black loading smaller than in another device, this would indicate a comparatively better performance. As the purpose of this study is to "situate" the minimixer in relation to existing laboratory mixers and industrial research twin screw extruders in general, this is a key test. These experiments had the merit that conductivity measurements of a sample of extrudates obtained from different machines were sufficient to assess performance. Chart 4.9 shows the resultant plot of resistance versus concentration at various mixing speeds for the minimixer.

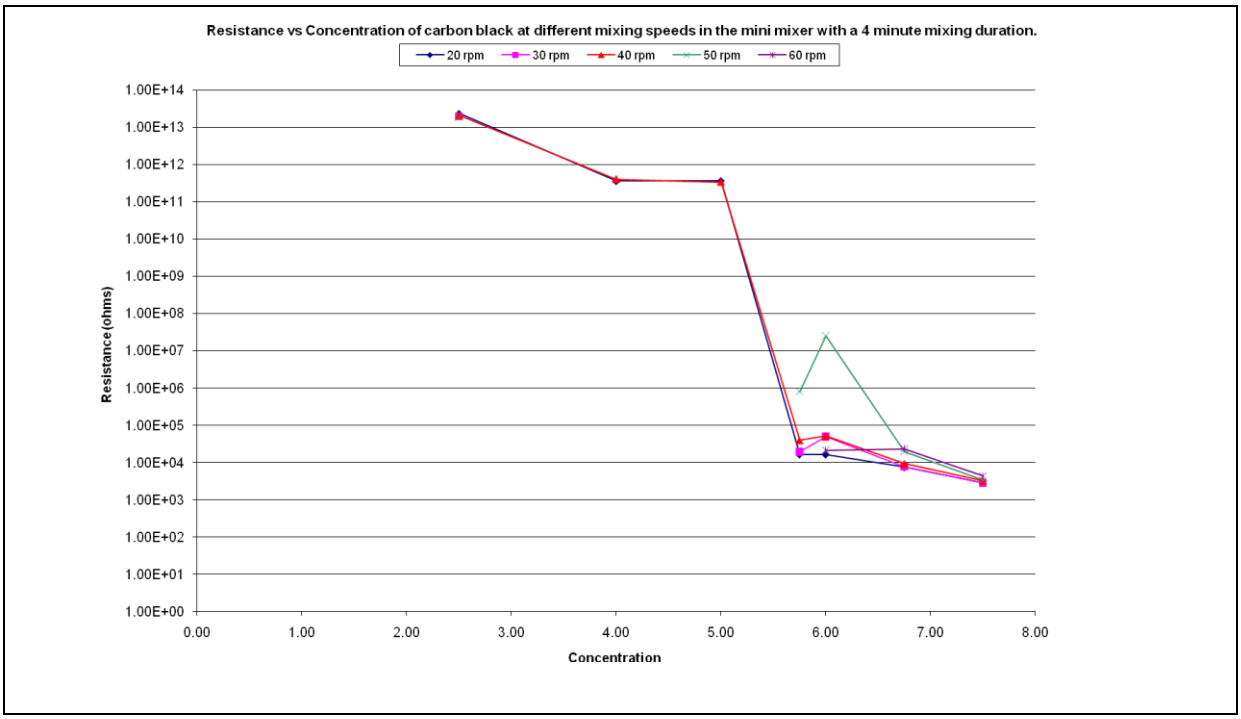


Chart 4.9 Mini Mixer Resistance versus concentration at 4 minutes mixing.

It can clearly be seen that between a carbon black concentration of 5% and 6%, the polymer goes from being an insulator to semi-conductive. From this chart the effect of mixing speed on the resultant resistance of the sample is hard to determine. Therefore by plotting the resistance against speed for each concentration, this effect can be seen and is shown in Chart 4.10 and shows that speed has some effect but not greatly. This would indicate that either reaching the semi-conductivity threshold is independent of mixing speed and therefore shear rate, or that the mixing has been achieved during the period of manually charging the material to the mixer. This charge period could take between 1 to 2 minutes due to the powdered nature of carbon black and the difficulty of charging this with the polypropylene pellets. During which time the mixing elements and screw are constantly turning and causing a mixing and melting action.

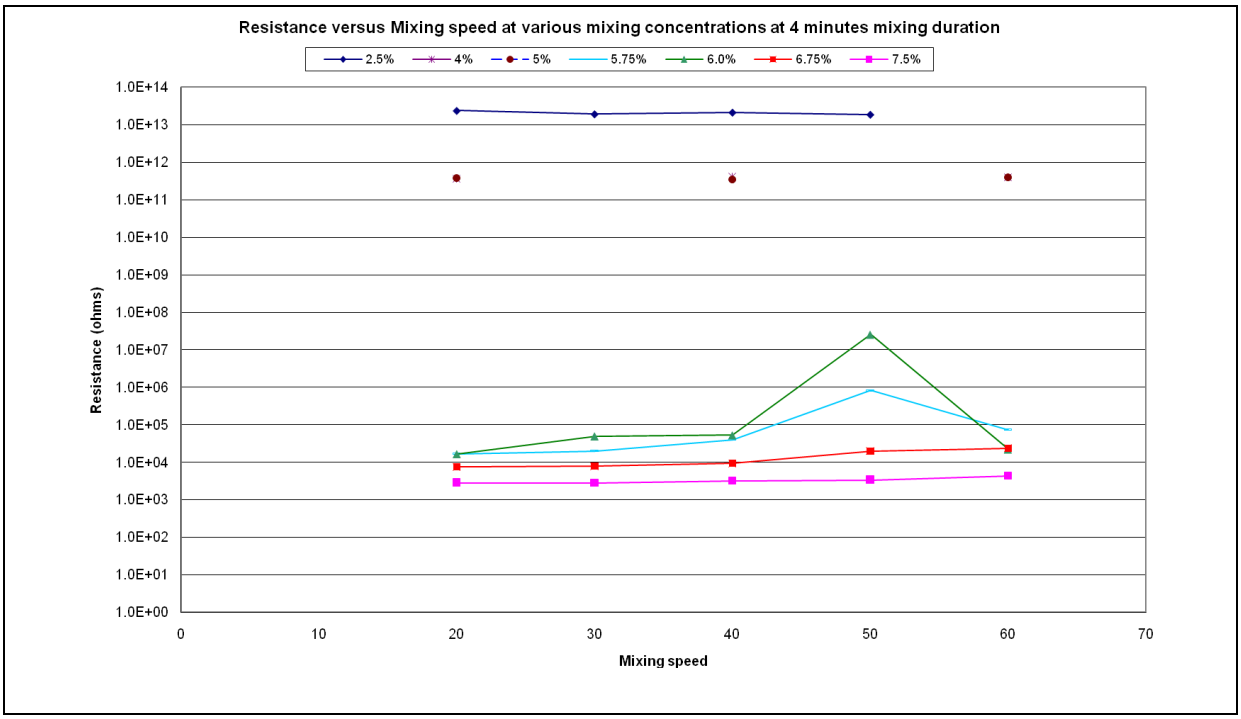


Chart 4.10: Mini Mixer Resistance versus mixing speed at 4 minutes mixing.

A short trial was conducted looking at a residence time of 2 minutes at the slowest and highest speeds previously used, starting at a concentration 2.5% carbon black and increasing

to 7.5% carbon black, the results of which are shown in Chart 4.11. Like the previous experimental data they show a similar pattern, where speed seems to have a negligible effect on the change in semi-conductivity. But show that the threshold is reached between 5% and 5.5% carbon black. This would suggest that the residence time inside the mixer has some effect and that too long could be detrimental at concentrations close to the percolation threshold.

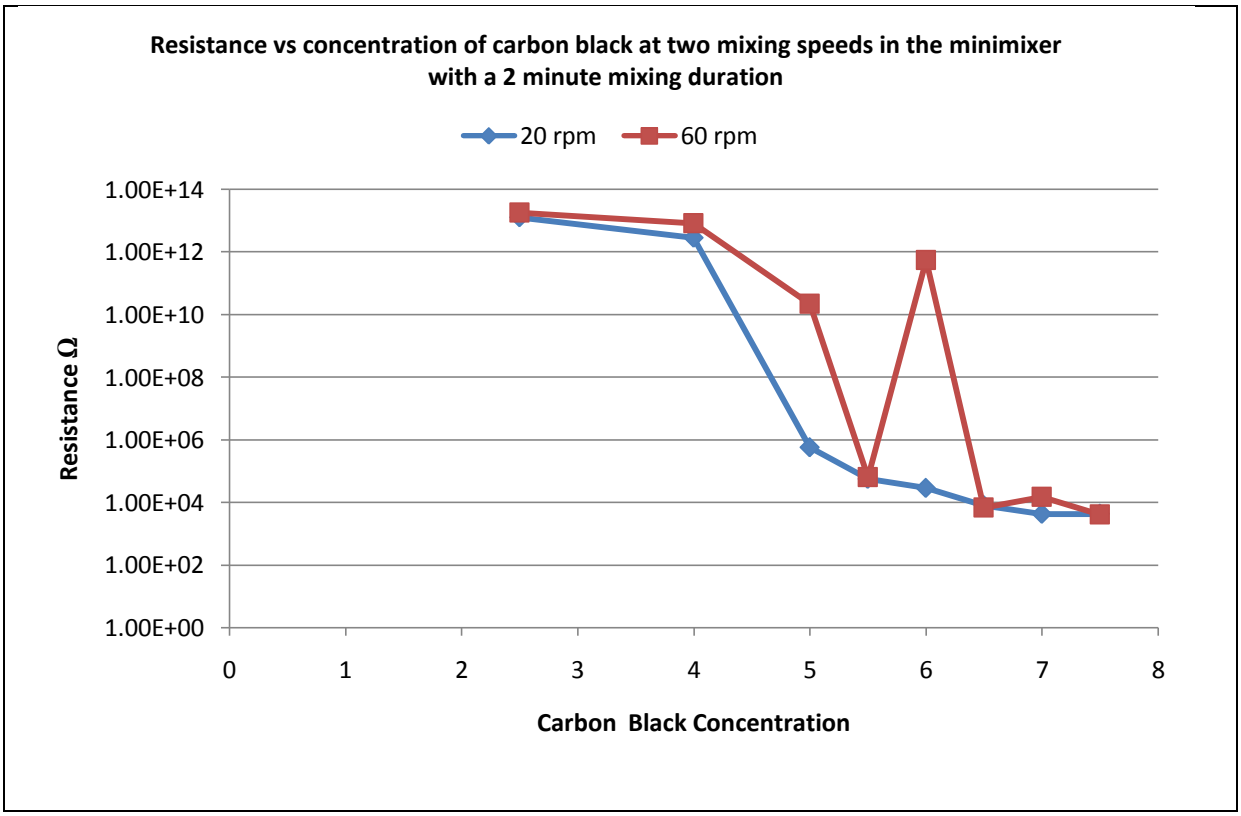


Chart 4.11 Mini Mixer Resistance versus Concentration at 2 minutes mixing

Using this as our basis for the Mini mixer, the results from the Haake were then plotted in comparison and are show in Chart 4.12 and Chart 4.13. In Chart 4.12, it seems that at the lower speeds for the 1 minute mixing duration, the mini mixer performs better, but this role is reversed at the higher speeds with the Haake as it begins to produce semi conductive samples at the 5% concentration value. When the mixing duration of the Haake is increased to that of 4 minutes, the Haake again seems to perform better than the mini mixer, again

producing semi conductive samples at 5% concentration. This would seem to suggest that the Haake is proving to be more successful at dispersing the carbon black pigment throughout the high MFI polymer. Again like the minimixer the affect of speed on where the conductivity threshold concentration is reached appears negligible. Like the mini mixer the charging of material to the Hakke could take between 1 to 2 minutes due to the difficulty in charging the carbon black powder, during which time the screws are in operation and some material is re-circulating through the device

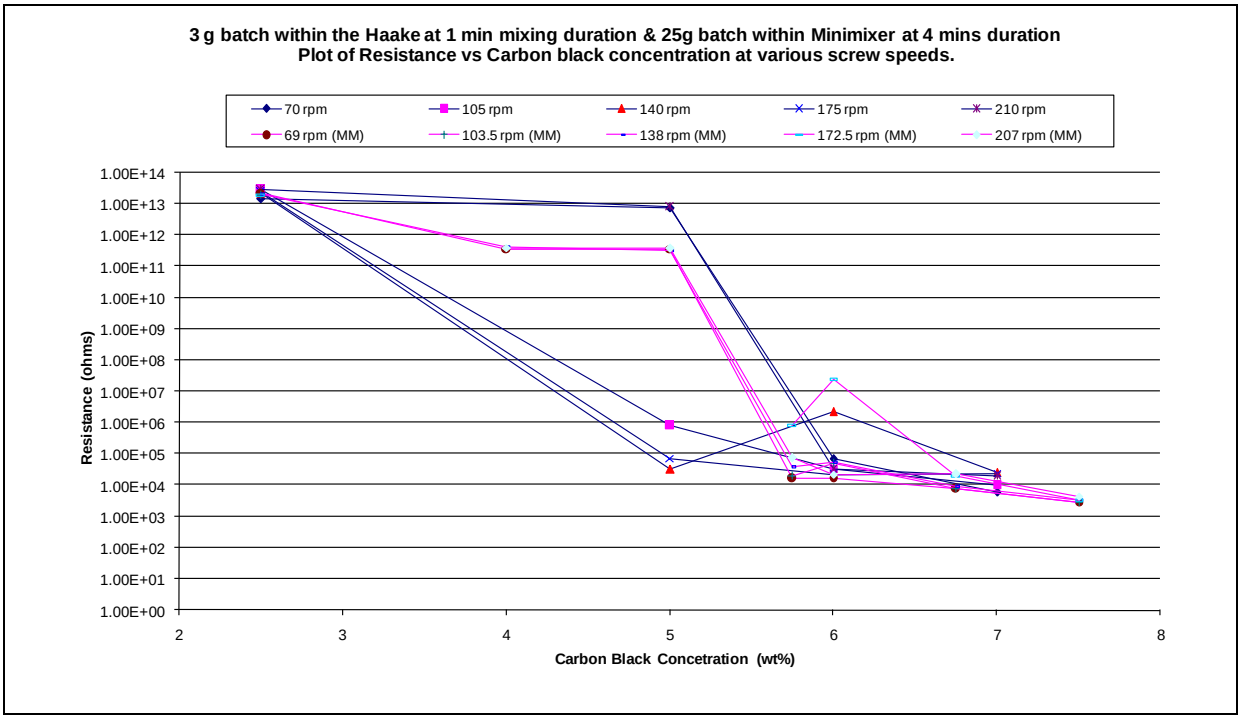


Chart 4.12 Comparison between Mini mixer and Haake Rheomex

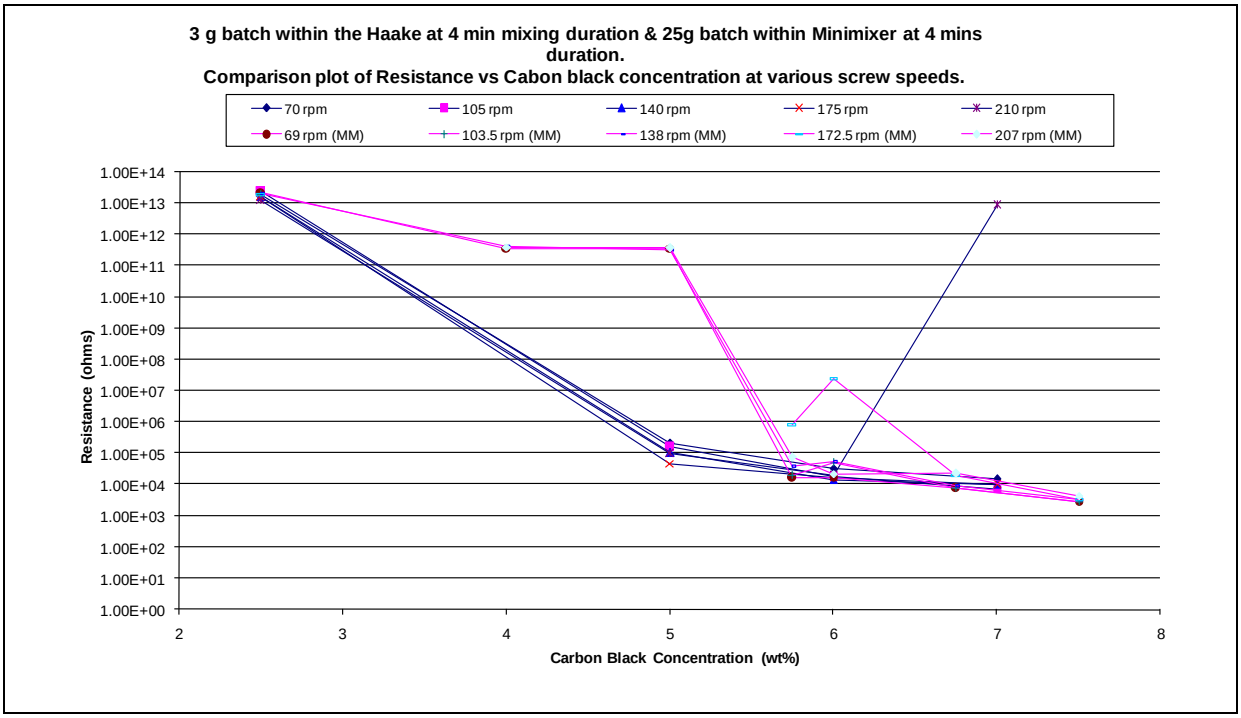


Chart 4.13 Comparison between Mini mixer and Haake Rheomex

Scaling up to the 19mm APV twinscrew extruder offered different challenges. This machine operates in a starved feed condition, but due to the quantities of carbon black involved, it was necessary to fix the feed rate of carbon black into the twin screw and alter the feed rate of polymer to vary the concentration. This would suggest that the minimixer out performs the machine, which seems to struggle to produce any sample with semi conductive properties below a concentration of 7%, as can be seen in Chart 4.14. The basic geometries between the two machines are similar, such as cams to provide the mixing as material flows through the system. Unlike the minimixer, both materials are fed simultaneously and continuously into the extruder. But the arrangement of the elements in the twin screw may have been the contributing factor, as there is a long screw section to allow the polymer to melt fully before entering the first section of mixing elements. This differs from the mini mixer arrangement as material is charged directly into the mixing cavity, allowing the

polymer pellets to partially melt and begin to mix with the carbon black additive during charging.

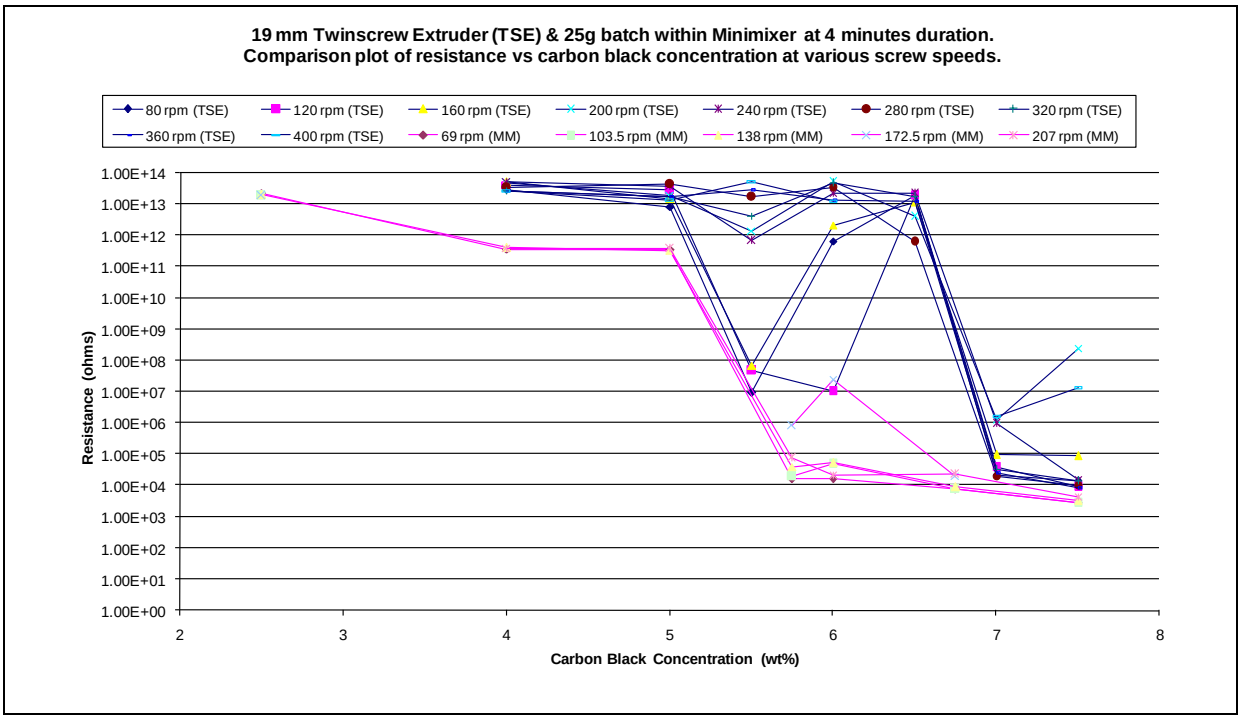


Chart 4.14 Comparison between APV twinscrew and Mini mixer

Finally the 40 mm Betol Twin screw extruder was compared and at four different feed rates since the machine operates under a starved feed condition much like the 19mm APV, but because of the quantities polymer being used it was possible and more sensible to vary the concentration of Carbon black being added to the twin screw. Chart 4.15 shows that at the 3 kg/hr feed rate of polymer into the machine, that the twin screw seemed incapable of producing a sample that was semi conductive. This could be easily explained by considering that the quantities of material being fed to the system were insufficient to create a condition where the barrel could be considered full with molten polymer until right before the die. This idea is supported by the fact that as the feed rate of polymer was increased; the twin screw began to produce samples with semi conductive properties. Chart 4.16 demonstrates that at a polymer feed rate of 5 kg/hr the two machines performed almost

equally well. As the feed rate of polymer was further increased the Betol twin screw demonstrated that it could outperform the mini mixer, easily producing semi conductive samples at almost all concentrations, see Chart 4.17 and Chart 4.18.

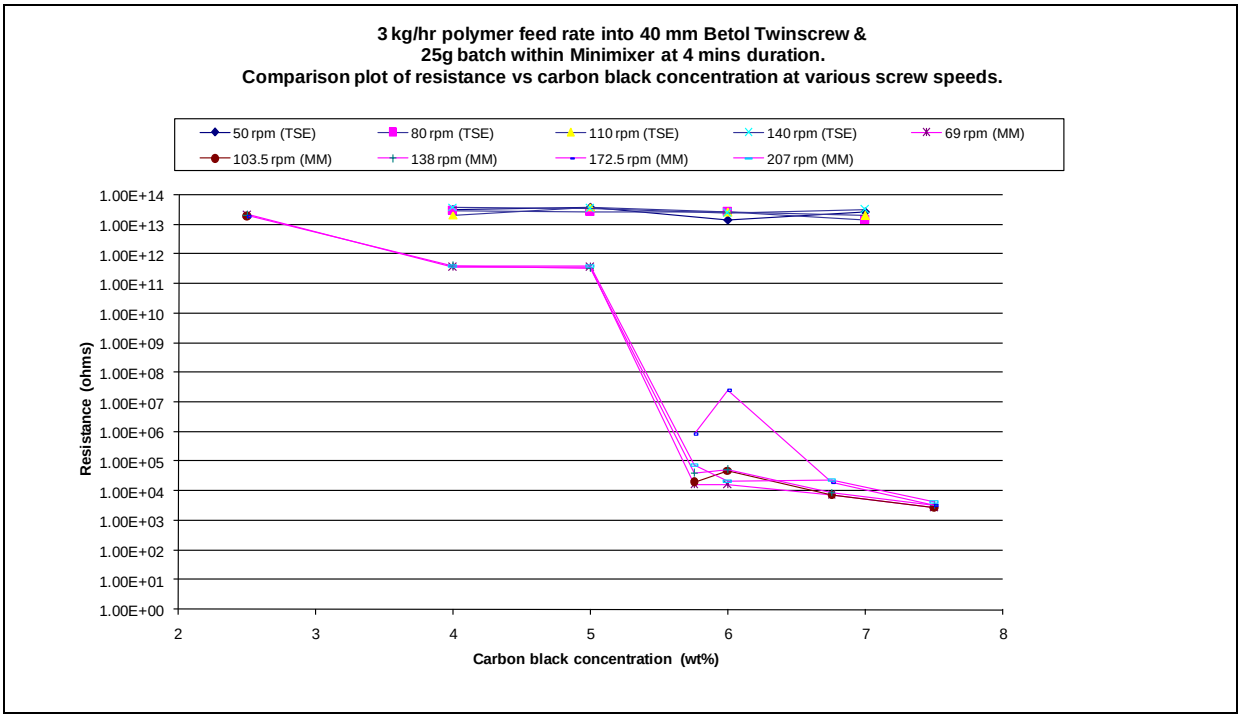


Chart 4.15 Comparison between Mini Mixer and 40mm Betol running at 3kg/hr

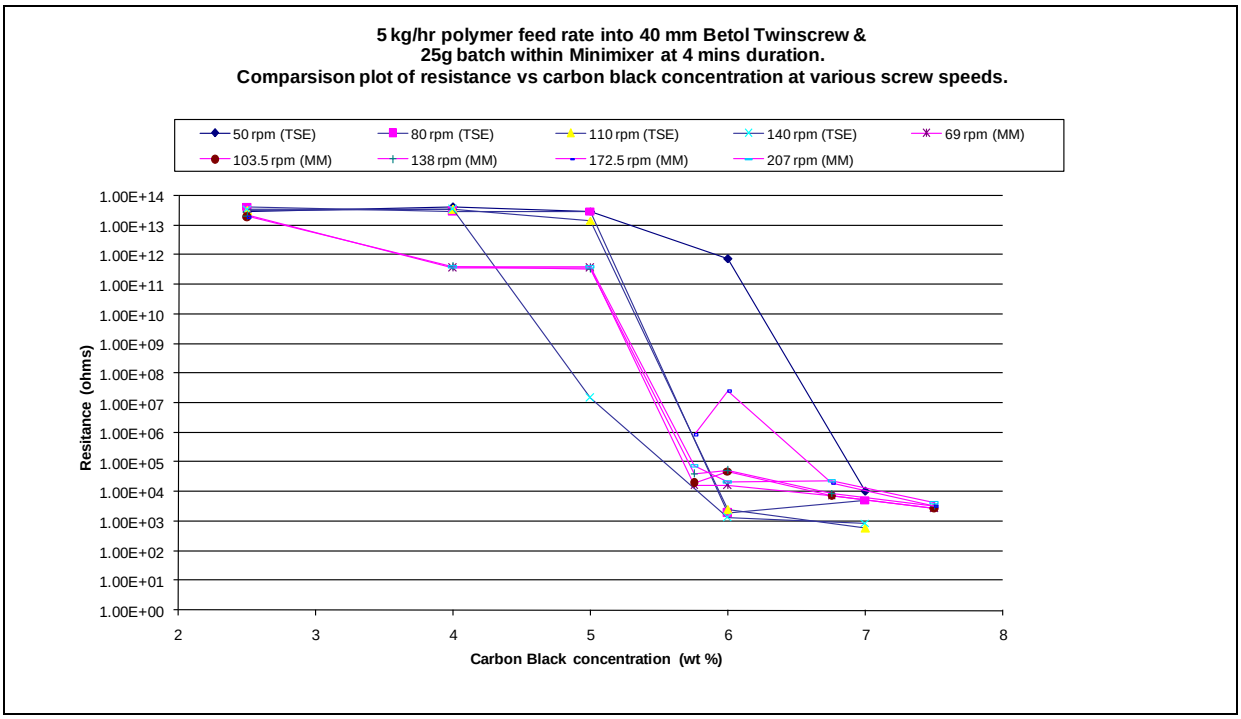


Chart 4.16 Comparison between Mini Mixer and 40mm Betol running at 5kg/hr

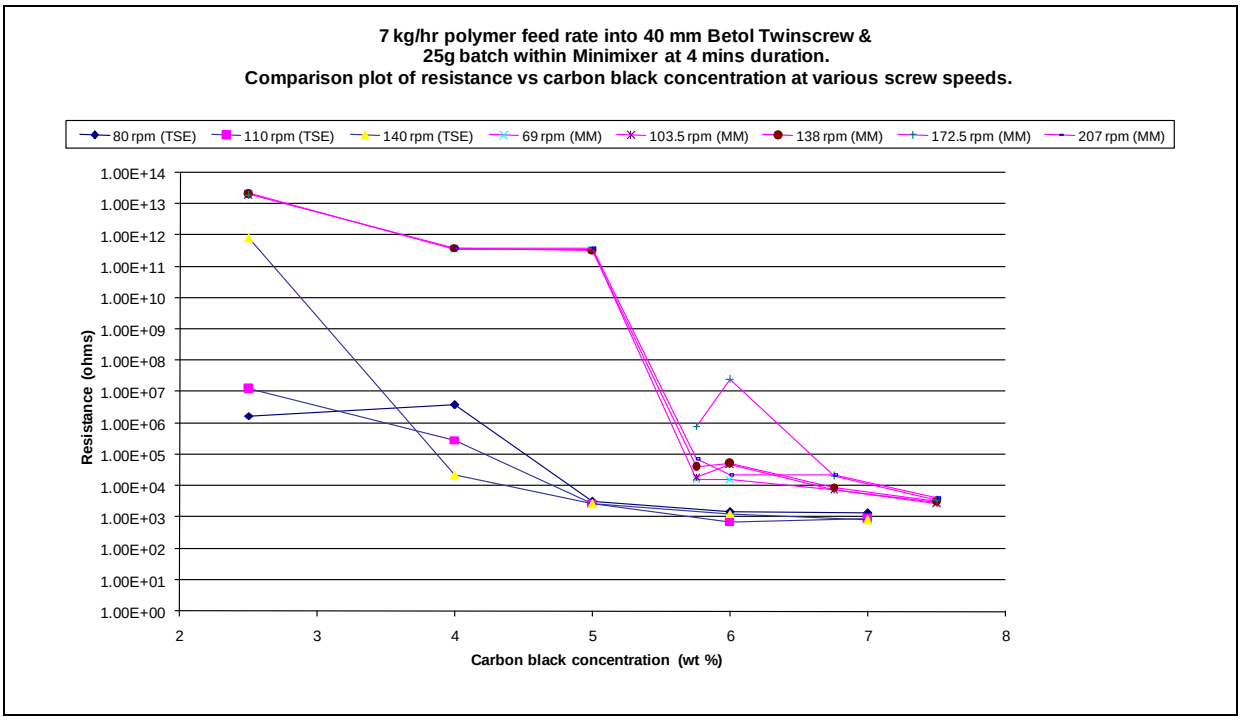


Chart 4.17 Comparison between Mini Mixer and 40mm Betol running at 7kg/hr

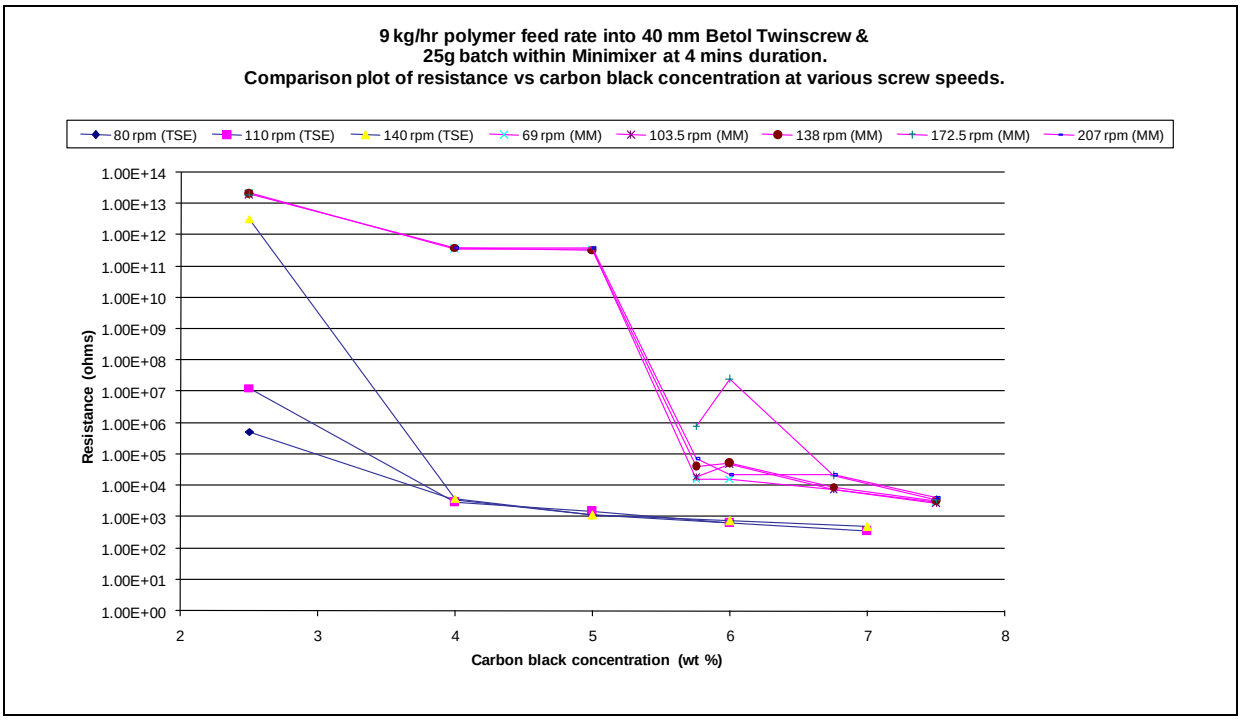


Chart 4.18 Comparison between Mini Mixer and 40mm Betol running at 9kg/hr

This clearly shows that the feed rates entering a twin screw and how ‘full’ the screws are of molten polymer affects the performance of the machine. This concept is not new and quite logical as you would expect the machine to operate at its peak performance when the using the maximum through put possible.

This out performance of the twin screw over the mini mixer may also come down to the geometries of the mixing elements, as the betol twin screw made use of a closely intermeshing trapezoidal screw arrangement with sections of tri-lobal and barrier mixing elements. This suggests that an investigation into the different mixing element types within the mini mixer would be important further work.

4.7 Conclusions

From the colour matching experiments the results were not satisfactory in assessing the mixing capabilities of the mini mixer. The standard provided the industrial collaborator Colloids Ltd was poor and the technique qualitative and therefore unsuitable.

The Americhem experiments were more informative, showing a clear improvement in dispersive mixing as time and speed was increased. This increase appeared to be almost linear in relationship. Indicating that the minimixer is able to effectively disperse the americhem additive.

The carbon black comparison trials are difficult to derive conclusion from. They indicate that mixing speed and duration in the batch devices (Mini mixer and Hakke), have little effect on the achievement of the semi-conductivity threshold. Due to the duration of charging to these devices, it can be concluded that this may have a significant effect and needs more careful consideration in which materials are used and how they are charged.

The comparison to the larger scale machines are also difficult to draw conclusions, and would indicate that the use of Carbon black as a method of measuring mixing performance through an intrinsic property of the material was theoretically sensible but in practice not as desirable. Therefore another approach needs to be considered.

Chapter 5: Recommendations for future Work

5.1 Introduction

The work done to achieve the objectives of the research has been presented and based upon that work; I now put forth in this section, proposals for further research and development of the Mini Mixer.

5.2 Modelling of the flowpath inside the mixer

From the experimental study we know that the mini-mixer is an effective tool for dispersive and distributive mixing. We also have a reasonable idea on how material moves within the mixer, but we cannot fully visualize this flow path of the particles clearly. Being able to do this would be of great benefit in the flow path modelling process.

One of the ways to help visualize this process would be through the use of a transparent barrel e.g. Glass or Perspex. With this in mind a Perspex barrel was initially made and a number of cold liquids (Gelatine, Honey, Silicone oil) were tested in order to see we could visualise the flow path. Unfortunately there was not enough time to perform a complete and detailed study. The observations made were outlined in Chapter 4.They clearly show how the fluids moves during discharge and mixing, although at the time a suitable tracer had not been found for the brief study.

The biggest challenge is to find a suitable cold liquid that mimics the properties of a polymer melt and also finding a suitable tracer, be it dye or some particulate, so that the mixing

process can be observed clearly. The work by Sernas [37] may give an indication of a suitable cold fluid that can be used in the form of clear corn syrup. These observations should then aid in the generation of a computer model of the mixing chamber of the Mini Mixer through the use of FLUENT or POLYFLOW software, which is available at the University of Bradford. From this simulation work investigations into different mixing element geometries could be done to assist with determining the optimal arrangement for mixing flows within the machine. Due to the design of the mini mixer and its ability to have interchangeable mixing elements, practical studies could then be conducted to confirm the results of the computer simulations.

5.3 Alter position of feed port and replacement of hexagonal paddles.

Currently the feed port is above two pairs of hexagonal paddles which are there to sweep material down onto the screw. In practice these paddles have a tendency to sweep material up into the feed port during operation, forcing the plunger out if it is not weighed down and locked in place.

In the operation of normal twin screw and single screw machines, feeding material onto such paddles does not exist or if it does, in very rare circumstances. Material is always fed directly onto the screw and pellets allowed to melt as they are transported down the barrel to where the mixing cams are found. Therefore by extending the screw length and replacing the hexagonal paddles with the regular mixing elements, it is possible to feed directly onto the screw and have a melt zone for the polymer, in which the melt is then conveyed into the mixing cavity. This should stop material being forced up into the feed port during mixing and have the added benefit of making it easier to manufacture the barrel of the mixer and any Perspex version used for visualization trials.

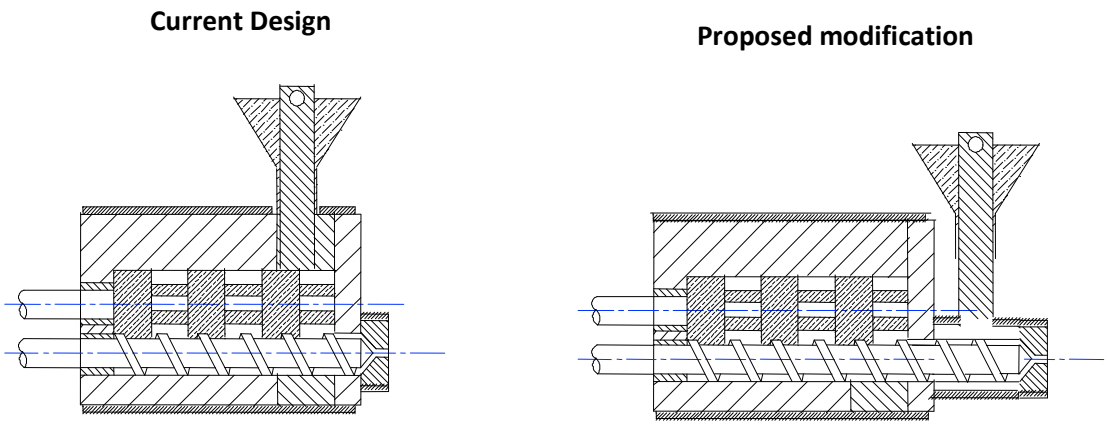


Figure 5.1: Proposed feed port modification

This will require the plunger to be locked in place during discharge to prevent material exiting via the charge chute. Most importantly this new arrangement makes available two additional pairs of mixing elements (cams) which will provide extra mixing length. The arrangement would also give polymer pellets some time to melt before reaching the mixing cavity and causing jarring of the machine. This may also alleviate the issue of charging material to the mixer that was highlighted in the carbon black experiments.

5.4 Cleaning issues

The existing arrangement for opening and closing the barrel of the mixer consists of a rack & pinion system. Although this is sufficient, it is a hindrance when it comes to cleaning the mixers internals. It does not extend the barrel far enough to be able to clean the mixing cavity without the risk of burning your hands. This has made it necessary to dismount the barrel from the rack & pinion system for cleaning which can be difficult while wearing heat protective gloves.

In order to overcome this it would be better to have the barrel opening mechanism mounted underneath.

This would make it easier to access the mixing elements and screw, it would also be possible to rotate the barrel through 90° to make it easier to clean the mixing cavity in the barrel. Also, the faceplate of the barrel can be made so that it can easily be removed, making the cleaning of the barrel much simpler. This is not possible with the existing system as the faceplate is used to mount the barrel onto the rack and pinion system.

One of the problems with existing mixer is that there is quite a large heat loss from the mixer back plate. This heat loss causes material to solidify around the shafts near the last pair of mixing cams. This causes problems with closing of the mixer barrel effectively and as a result extra time and effort is required to clean the back plate thoroughly so that an effective seal is made when the mixer is shut. This problem could be overcome by the mounting of a slim heating element, (Mica type or Spiral type), around the back plate.

5.5 Data logging

Although the mixer performs very well, there is no provision for automated logging of data such as temperature, speed, current and pressure. Also it is important to measure the torque required to carry out the mixing process. It is clear that the addition of fillers, masterbatches, etc changes the properties of the polymer composite. This in turn would change the torque required to drive the mixer. Therefore a torque transducer installed may possibly give data from which other material properties could be inferred.

In order to carry out data logging, it is possible to purchase hardware and software from different sensor suppliers/vendors and have the signals from these synchronized in a one piece of application software. A more preferable method would be to use hardware and software from a single specialized vendor, e.g. National Instruments. This would eliminate the need for synchronisation since it would all be done automatically by the vendor software e.g. National Instruments Lab view software.

5.6 Design of a Sensing head for in-process measurements

One of the biggest problems with any mixing device is the time it takes to characterise (Tensile testing, X-ray diffraction, rheology measurements, etc.) the product. It would be useful to design a miniature slot die to carry out in process rheology measurements, similar to the dies designed for larger extruders. The advantage of this is that the measurements are made inline, whereas offline measurements would be subject to reheating of the polymer which sometimes degrades and changes the characteristics. The design of a mini slot die would have to take into account the relatively smaller pressures developed by the mini mixer screw compared to larger twin screw compounders. Miniature pressure transducers would have to be sourced for this application. The cross-sectional area would need to be the same as that of the normal strand die to keep the pressure/force requirements the same. Provisions should also be made for mounting other types of sensors e.g. ultrasound which is increasingly being used in the polymer industry to obtain gross property data.

5.7 Haul off system

In this study, the polymer exiting the mixer was hauled off by hand through a crude air ring giving rise to a strand of varying diameters. It would be better to use an automatic haul off system with speed control to ensure a uniform strand diameter. The speed control provides the option to set the what ever strand diameter you desire. This coupled with a more efficient air ring would be beneficial especially when operating at temperatures higher than 240 Deg C.

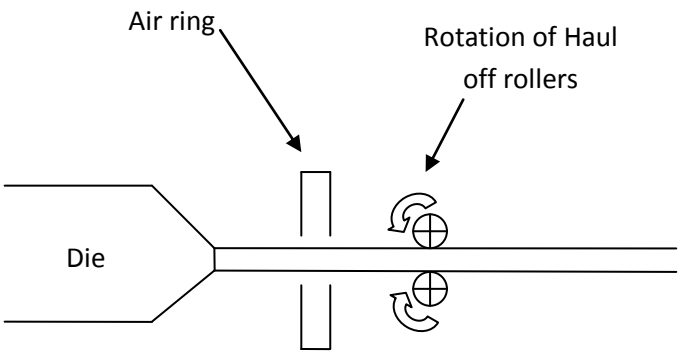


Figure 5.2: Proposal for a haul off system

5.8 Die swell measurements.

It is known that some additives alter die swell, de-stressing the material to some degree and it would be useful to measure this effect and compare this to different properties of the material.

In the minimixer, die swell can easily measured by mounting a CCD camera at 90º to the die. Instead of using a haul-off, the material should be allowed to flow over a rod and onto the base. The diameter of the strand just before the rod should be used to compare the degree of die swell. The ratio of the strand diameter to the die diameter can be used to compare with other material properties such as tensile strength, viscosity etc.

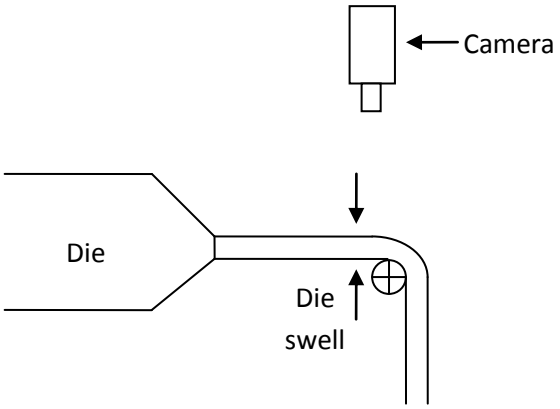


Figure 5.3: Die swell measurements

Sometimes a correlation can be found which makes it possible to make quick predictions of material properties by just monitoring the effects of die swell.

5.9 Final Conclusions

The mini mixer is a device useful for mixing additives into small quantities of polymer (10g – 25g) for producing samples for characterisation. The most comparable commercial mixer is that of the Hakke Rheomex, but that's the disadvantage of only producing 1 or 2 grams of material, which is not sufficient for some characterisation techniques as the quantity is too small and runs the risk of material re-agglomeration or degradation in the re-circulation channel. The mini mixer offers an alternative that processes material on the grams scale, but able to provide sufficient material for characterization techniques that require more than just 1 or 2 g of material.

Rheomex → 2-4g per run, so may need something in the region of 10 runs.

Mini Mixer → 10-25g per run, so may need only 2 runs.

TSE → 1 kg/hr upwards. So not as useful if you only have small quantities available.

Future work is necessary to study the mixing process using mathematical modelling procedures such as Computation Fluid Dynamics (CFD). The university has access to Fluents Fidap and Polyflow software and one of these should be used to compare with data obtained from a thorough study with a transparent barrel. A good understanding of how to visualize the mixing action within the mixer barrel is necessary, before further investigation into comparing the device with larger scale machines should be conducted.

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Appendix

The appendix CD contains the visualization videos and the raw data collected by OPTIMAS for the Americhem experiments. The raw data for Carbon Black experimental results is also contained on the CD.

Appendix A: Americhem Sample Images

Scale: 4 mm wide by 3 mm high